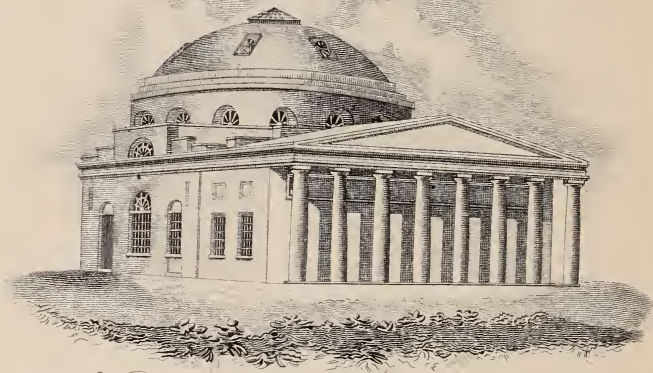




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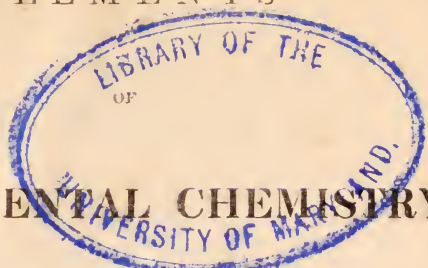
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THE  
ELEMENTS

EXPERIMENTAL CHEMISTRY,



BY

WILLIAM HENRY, M.D. F.R.S.

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THE ELEVENTH EDITION,

COMPREHENDING ALL THE RECENT DISCOVERIES; AND ILLUSTRATED WITH TEN PLATES BY LOWRY, AND SEVERAL ENGRAVINGS ON WOOD.

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IN TWO VOLUMES.

VOL. II.

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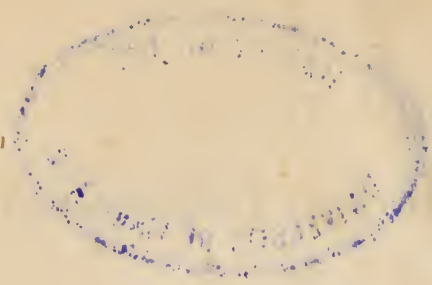
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LONDON:

PRINTED FOR BALDWIN AND CRADOCK, PATERNOSTER-ROW.

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ELEMENTS  
OF  
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CHAPTER IX. (*Continued.*)

OF METALS.

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SECTION XIV.

*Manganese.*

MANGANESE never occurs in a metallic state as a natural product. The black substance, known in commerce by that name, the composition of which was first discovered by the illustrious Scheele, is a compound of manganese, and the largest proportion of oxygen, with which that metal is capable of uniting, without being acidified. It is, however, by no means a pure peroxide of manganese; for it contains not only carbonates of lime and baryta, the oxides of iron, copper, and lead, but occasionally a little sulphate and muriate of lime. The last-mentioned substance, by affording chlorine on the addition of sulphuric acid, has led to the erroneous opinion that chlorine is always present in the native peroxide.

*Purification.*—The native peroxide, finely pulverized, may be first well washed with boiling distilled water, and dried; then intimately mixed with half its weight of muriate of ammonia, and heated to redness for a short time in a crucible. The chlorine, which is disengaged, seizes the manganese in preference to any other metal; and, by washing the residue with water, a solution of pure muriate of manganese is obtained. From this solution, bi-carbonate of potassa throws down a pure

carbonate of manganese, which may be converted into protoxide by exposing it, ignited in a green glass tube, to a current of hydrogen gas. In preparing the salts of manganese, it is sufficient to dissolve in acids the carbonate itself, which may be considered pure if it leave no residue, and afford perfectly colourless solutions. This process is due to Mr. Faraday. (Quart. Journ. vi. 358.) If a little iron be present along with manganese in any solution, the iron may be separated, as Mr. Hatchett long ago showed, by ammonia, which throws down the oxide of iron, and forms with the manganese a soluble triple salt. (See the chapter on Mineral Analysis.)

Dr. Turner employed the following method of preparing the carbonate, as a source from which he might obtain, in a pure state, the oxides and other compounds of manganese. The dark brown mass, left in the process for procuring oxygen gas by heat from the common peroxide, was mixed with a sixth of its weight of powdered charcoal, and exposed to a white heat for half an hour. The protoxide thus formed was dissolved by muriatic acid, the solution evaporated to dryness, and the residue kept for some time in a state of fusion at a red heat. The resulting chloride of manganese was redissolved by distilled water; and, after being filtered, was found to contain no impurity except a little lime, which was separated by oxalate of potassa. The manganese was then precipitated by a solution of the bi-carbonate of potassa, and the carbonate of manganese, after being carefullyedulcorated, was laid on a filter. After removing the upper layer, which had become rather brown by exposure to air, the white carbonate was kept in a vacuum along with sulphuric acid, till it became perfectly dry. The salt thus prepared dissolved entirely in dilute sulphuric acid, and gave a colourless solution. (Edinb. Phil. Trans. 1828.) Of these two methods, I have practised the first only, with which I have found every reason to be satisfied.

*Metallization.*—From the protoxide, metallic manganese may be obtained by mixing it, after being finely powdered, with pitch, making it into a ball, and putting this into a crucible with powdered charcoal, one-tenth of an inch thick on the sides, and one-fourth of an inch deep at the bottom. The empty space is then to be filled with powdered charcoal, a cover is to be luted on, and the crucible exposed, for one hour, to the strongest heat that can be raised. Mr. Faraday has succeeded

in obtaining metallic manganese in large globules from the triple tartrate of manganese, by heating it *per se* in a crucible placed in a wind furnace.

This metal is of a dusky white colour, and bright and shining in its fracture. Its specific gravity was found by Dr. John to be 8.013. It is very brittle, and even more infusible than iron, requiring a heat of 160° Wedgwood to melt it. It is not attracted by the magnet, except when contaminated with a small quantity of iron. When exposed to the air, it soon crumbles into a blackish brown powder, in consequence of its oxidation, and becomes in succession grey, violet, brown, and finally black.

*Oxides of Manganese.*

Considerable labour has been employed by chemists in the investigation of the oxides of manganese, a subject of greater difficulty and obscurity than might have been supposed. These oxides may now, however, be considered as reduced within the general laws of atomic combination. This has been progressively effected by the inquiries of John, Berzelius, Forchhammer, Berthier, Arfwedson, Thomson, and Turner; of which I shall offer a condensed view.

To the experiments of Dr. John it may be sufficient to refer the reader (see Thomson's *Annals of Philosophy*, vols. i. and ii.); because, though good approximations for the time when they were made, yet they have been superseded by results of greater precision.

Berzelius was led by his researches (*Ann. de Chim.* lxxxvii. 149), to admit the oxides enumerated in the following table:

*Berzelius's Table of the Composition of Oxides of Manganese.*

	Metal.	Oxygen.	Métal.	Oxygen.
1st oxide .....	93.435 ..	6.565 ....	100 .....	7.0266
2d oxide .....	87.68 ..	12.32 ....	100 .....	14.0533
3d oxide .....	78.10 ..	21.90 ....	100 .....	28.1077
4th oxide .....	70.50 ..	29.50 ....	100 .....	42.16
5th oxide .....	64.00 ..	36.00 ....	100 .....	56.215

The experience of Gay Lussac (*Ann. de Ch. et de Ph.* i. 39), led him to the conviction that the two first oxides do not exist; and that there are in reality only three; 1st, the *protoxide*, obtained by dissolving manganese in diluted sulphuric acid, and precipitating it by a pure alkali out of the contact of air; 2d, the *deutoxide*, which remains after calcining the *peroxide*,

or the greater part of the salts of *manganese*; and 3d, the *peroxide*, or native black oxide. And Berzelius himself, at a subsequent period, relinquished the two first (Ann. de Ch. et de Ph. v. 150), and now admits only three oxides of manganese, with quantities of oxygen corresponding to the three last in the above table; the protoxide (the 3d of the above table) being green, and the two others black. Besides these, there is also a *red oxide*, in which 100 parts of manganese are united with 37.47 oxygen. But this, not agreeing with the law of definite proportions, he considers as a mixture of the two first. (Ann. de Ch. et de Ph. vi. 204.)

An able investigation of the oxides and salts of manganese was published by Dr. Forchhammer in 1820, in an inaugural dissertation, "De Mangano," of which an abstract may be found in the Annals of Philosophy, vols. ii. and iii.

1. To obtain the *protoxide*, a glass tube, open at both ends, was filled with deutoxide, and heated over a lamp, or over ignited charcoal, while hydrogen gas was passed through it. The brown powder soon changed to a light yellow, which colour, while the powder was cooling, became white, and the powder, when cold, was of a beautiful light green. Its colour, however, soon changed by exposure to the air, and, when heated below  $600^{\circ}$ , it was reconverted into deutoxide, burning slowly with a reddish light. The same process was afterwards employed by Arfwedson, who obtained the protoxide of a fine pistachio green, which, on the admission of air, became greyish green. When heated in a glass capsule over a lamp, it took fire, and burned into a dark brown oxide, 100 parts becoming 107.35. Dr. Turner had recourse to the same method of preparing the protoxide, the purity of which he ascertained by its being entirely soluble in dilute sulphuric acid, and giving a colourless solution. The colour of the pure protoxide he describes as mountain green, and considers a darker tint as indicating an admixture of *red oxide*. He found that the protoxide did not absorb oxygen by exposure, during nineteen days, to the open air; that at  $400^{\circ}$  Fahr. it absorbed oxygen very slowly, but more rapidly at  $600^{\circ}$ , and was then converted into red oxide. The combustion, noticed by Forchhammer and Arfwedson, did not occur in his experiments, but that it generally takes place I can add my testimony to theirs. The protoxide, it is agreed on all hands, is the only oxide which forms definite compounds



with acids. These, according to Dr. Turner, are essentially colourless, their reddish tint being due to a minute quantity of red oxide.

2. The *deutoxide*, according to Forchhammer, may be obtained by exposing the pure carbonate of manganese, during a long time, to a rather low red heat in an open vessel; or, by triturating peroxide of manganese with binoxalate of potassa and water, a pink solution is obtained, from which ammonia throws down the deutoxide. Its colour is brown, resembling that of deutoxide of iron, but rather darker; it varies also with the source from which it has been derived. That procured by heat, from the native peroxide or hydrated deutoxide, has a brown tint; but, when prepared from the nitrate of manganese, it is almost as black as the peroxide itself; and the native deutoxide is of the same colour. It is soluble in concentrated muriatic acid at 42° Fahr.; but, if the temperature of the solution be at all raised, or if it be exposed to the sunbeams, chlorine escapes, and muriate of protoxide is formed. The existence of the deutoxide has been doubted, but, according to Dr. Forchhammer, it is the only one which can be easily obtained in a pure state. Arfwedson has since recognised it as forming, combined with water, the grey ore of manganese; and Dr. Turner has demonstrated it in two different states of combination in the mineral kingdom, *viz.*, as an oxide and as a hydrate, the latter constituting the mineral called *manganite*.

3. When the deutoxide is boiled with weak nitric acid, a portion of it parts with oxygen, and enters into solution in the state of protoxide, while the remainder is converted into *peroxide*, which is black, and insoluble in all acids except such as deprive it of oxygen. On evaporating the nitric solution, and heating the product to redness, *peroxide* is left, which, however, if not sufficiently heated, still holds a little nitric acid; and, if too strongly, parts with a little oxygen. Owing to this uncertainty, Dr. Turner does not rely on artificial peroxide for purposes of analysis.

From a careful analysis of the native *peroxide of manganese*, Dr. Turner concludes, with other chemists who have recently studied it, that it contains exactly twice as much oxygen as the protoxide. It is, accordingly, constituted of 28 metal + 16 oxygen, and, by being converted, at a white heat, into red oxide, should lose 12.122 per cent. of oxygen gas. Heated

with concentrated sulphuric acid, 44 parts yield 8 of oxygen, and 36 of protoxide unite with the acid. It appears, however, that there are deviations from the uniformity of the proportions composing native ore of manganese. The Warwickshire ore, for instance, first observed by Mr. Phillips to be anomalous, is, in Dr. Turner's opinion, a mixture of the hydrated deutoxide and anhydrous peroxide. (Ann. of Phil. March and April 1829.)

Berthier (Ann. de Ch. et de Phys. xx. 186) contends that manganese has four degrees of oxidation, besides that which constitutes manganic acid. 1st. The *protoxide*, obtained by exposing to a white heat, in a charcoal crucible, either the carbonate or any pure oxide of manganese. 2dly. The *deutoxide*: this, he admits, by the action of concentrated nitric acid, is resolved into the protoxide which is dissolved, and the peroxide which remains. 3dly. *The red oxide*, which results from the calcination either of the deutoxide or peroxide. It consists of 100 manganese united with 36.24 oxygen, or supposing, as Berthier thinks probable, that the oxygen is a little underrated, it may be constituted of 2 atoms of protoxide and 1 atom of peroxide. 4thly. The *peroxide*, obtained by calcining the nitrate carefully to a certain point, and found also native in a crystallized form. By being heated in a charcoal crucible, 100 grains of a very pure specimen gave 76.9 grains of protoxide.

The researches of Arfwedson (Ann. of Phil. N. S. vii. 267,) were principally directed to the analysis of a brown oxide of manganese, obtained by calcining the protoxide, and heretofore confounded with that resulting from the calcination of the nitrate. Of this new oxide, he obtained 107.35 parts from 100 of the protoxide. But, in 100 parts of protoxide we have 77.78 of metallic manganese, and 22.22 oxygen, to which, if 7.35 oxygen be added, we shall find that in the brown oxide 100 of metal are united with very nearly 38 of oxygen. To this oxide Arfwedson applies the uncouth name of *oxidum manganoso-manganicum*. In composition, it agrees so nearly with the red oxide of Berzelius and Berthier, that it may be considered essentially the same. To bring the red oxide, then, within the law of atomic combination, it may be supposed to be constituted of

$$2 \text{ atoms protoxide} \dots\dots\dots 36 \times 2 = 72$$

$$1 \text{ atom tritoxide} \dots\dots\dots, 44$$

---


$$\text{Atomic weight} \dots\dots\dots 116$$

Or of

1 atom protoxide . . . . . 36

2 atoms deutoxide . . . . .  $40 \times 2 = 80$ 


---

 Atomic weight . . . . . 116

The *red oxide*, Dr. Turner has satisfied himself, is a uniform compound when it is prepared by calcining at a white heat the nitrate, the peroxide, or the deutoxide of manganese; and that it exists, as such, in the mineral kingdom. Its colour is variable, but when rubbed to the same degree of fineness, it is always of a brownish red colour when cold, and nearly black while warm. It does not change its state of oxidation by being ignited in contact with air. It dissolves in muriatic acid with a disengagement of chlorine, and communicates a deep red colour to the acid, which disappears on keeping. The mean result of its analysis by three different methods gave for its composition 92.951 parts of protoxide, + 7.049 oxygen, or 72.291 parts of metallic manganese + 27.709 oxygen. The numbers approximate so closely to those of Arfwedson, as to confirm the theoretical view of this oxide already given.

Mr. Dalton (New System, ii. 71) admits three oxides of manganese, the protoxide agreeing with that which is generally so termed; the tritoxide, or peroxide, he designates as the *deutoxide*, because it is constituted of 2 atoms of oxygen to 1 of metal; and to the oxide half-way between the two, he gives the name of *intermediate oxide*.

Dr. Thomson (First Princ. i. 364) satisfied himself by experiment of the composition of the protoxide, deutoxide, and tritoxide (peroxide). The colour of the deutoxide he finds to be either brownish black or shining black, according to the mode of its preparation, the first variety being obtained by exposing the peroxide to a low red heat, the second by calcining the nitrate. Both are identically the same, and give red solutions with sulphuric and muriatic acids, which are rendered colourless by sulphurous or nitrous acids. The existence of the first oxide of Berzelius's table he considers extremely doubtful, but sees no reason to doubt of that which stands second, though it must be considered as a *suboxide*, or compound of 2 atoms of metal and 1 atom of oxygen. The protoxide he regards, with Berthier, Arfwedson, and others, to be that which exists in the flesh-red sulphate, and which is obtained by exposing ignited

carbonate of manganese to a current of hydrogen gas. In this 100 metal are united with 28.5 oxygen, from which we may deduce the atomic weight of manganese to be 28; for 28.5 : 100 :: 8 : 28 very nearly. From this review, then, of the evidence of various experimenters, we consider the following compounds as sufficiently established:

*Oxides of Manganese.*

	Metal.	Oxy.	Metal.	Oxy.	At. Wt.
Suboxide . . . . .	100	14.286	28	4	32
Protoxide (green) ..	100	28.572	28	8	36
Deutoxide . . . . .	100	42.857	28	12	40
Tritoxide (black) . . .	100	57.144	28	16	44
Red oxide . . . . .	100	38.	28	10.6	

The *hydrated oxides of manganese* have been examined by Berthier, who has obtained chemical compounds of water both with the protoxide and peroxide, but has not reduced them to atomic proportions.

*Manganese with Chlorine, &c.*

Chloride of manganese may be formed by evaporating the muriate to dryness, and subjecting the residue to a red heat out of the contact of air. A pink-coloured semitransparent substance is obtained, which, according to the analysis of Dr. John Davy, consists of chlorine and manganese, in the proportion of 36 to 30.6. But the latter number exceeds the equivalent of manganese, derived from the analysis of its oxides. Dr. Turner has, therefore, again investigated this compound, and has discovered the error to consist in the partial decomposition of the chloride at a moderate heat. Avoiding this inaccuracy, he finds that 36 chlorine are united with 28.06 manganese, a number so near 28, that we may safely take the following to represent the true atomic weights of manganese and its chloride:

Manganese . . . . .	44	.. or	1 atom	28
Chlorine . . . . .	56	.. or	1 atom	36
				—
				100 Wt. of its atom
				—
				64

A new chloride (*per-chloride*) of manganese, remarkable for its volatility, has been discovered by Dumas, in which the chlorine is equivalent to the oxygen in manganic acid. (An-

de Ch. et de Ph. xxxvi. 81.) It is easily procured by mixing a solution of that acid, which will be described in the sequel, with concentrated sulphuric acid, and dry common salt. Water is formed, which is retained by the sulphuric acid, and chloride of manganese escapes in greenish or coppery-coloured vapours. By a cold of  $+ 5^{\circ}$  to  $- 4^{\circ}$  Fahr., it is condensed into a greenish brown liquid. When the air of a large tube is displaced by the gas, and this is poured into a larger tube, the interior of the latter being first moistened with water, a dense rose-coloured fume appears, and the inside of the vessel acquires a deep purple colour. This is caused by the instantaneous production of muriatic and manganic acids.

*Fluoride of manganese.*—This compound was first procured by Dumas, by a process similar to that employed in preparing the per-chloride, but it has since been more distinctly exhibited by Wöhler. Sulphuric acid is poured on the common chameleon mineral, previously mixed with half its weight of pulverized fluor spar. A great quantity of vapour is formed, of a fine reddish purple colour; and if the process be carried on in a small platinum retort, the neck of which is bent, so as to have its opening immersed in water contained in a cup of the same metal, the gas is absorbed, and the water assumes the reddish purple colour of a saturated solution of manganic acid, and becomes acid. The vapour, however, before absorption, is yellow when out of contact with air, which changes it to purple. Contact with glass decomposes the vapour, into manganic acid and fluosilicic gas. When brought into contact with dry chloride of calcium, great heat is produced, the fluoride of manganese is destroyed, and pure chlorine is disengaged.

The purple solution of the gas in water acts rapidly on copper, mercury, and silver, without any effervescence, and is rendered as clear and colourless as water; but it does not attack gold or platinum. It preserved its colour six months in a well-closed vial; but was rendered unfit for yielding manganic acid, and, when gently evaporated in a platinum vessel, gave oxygen gas and vapours of fluoric gas. (An. de Ch. et de Ph. Jan. 1828.)

*Salts, with base of Oxide of Manganese.*

*Carbonate.*—When a salt with base of protoxide of manganese is precipitated by a carbonated alkali, we obtain a snow-

white compound, which is a carbonate of manganese. When well washed and cautiously dried in a vacuum kept up by sulphuric acid, it is composed, according to Dr. Turner, of

Protoxide of manganese . . . . .	56.853
Water . . . . .	34.720
Carbonic acid . . . . .	8.427
	100.

This analysis agrees very nearly with Dr. Thomson's, but differs from that of Forchhammer, who seems to have been misled by supposing that the carbonate is converted into deut-oxide by calcination; whereas, in fact, the red oxide chiefly is formed. The water, not being in atomic proportion, Dr. Turner is disposed to think it probable that this salt may be strictly anhydrous.

*Sulphate of manganese.*—Concentrated sulphuric acid has very little action on metallic manganese; but the dilute acid dissolves it with an extrication of hydrogen gas, which has a peculiar smell, resembling assafœtida, probably from its holding some of the metal in solution. The solution has a light rose-colour, and gives crystals of the same colour.

The pure protoxide, and the carbonate of protoxide, dissolve in the sulphuric acid in any state of concentration; and a solution is obtained, exactly resembling that which has been described. The first crystals, that shoot from the solution, are of a faint flesh-red colour. The last are white, and contain a great excess of acid. The red crystals have the form of very flat rhombic prisms, and taste like Glauber's salts. They are soluble in 2½ parts of water, at 55° Fahr., and are insoluble in alcohol. The alkaline carbonates, prussiates, and phosphates, occasion a white precipitate from the solution, and are almost the only salts that decompose this sulphate.

Dr. Turner, by the synthesis of this salt, found that 19.01 grains contained 9 grains of protoxide, and 10.01 sulphuric acid, giving for the atomic weight of the protoxide 35.96, which is extremely near the number, as otherwise deduced. The salt, dried by being kept at a low red heat for an hour or longer, was white, and dissolved readily and entirely in distilled water. In its crystallized state it consists of

		Atoms.
Protoxide of manganese . . . .	30	. . . . 1 = 36
Sulphuric acid . . . . .	33	. . . . 1 = 40
Water . . . . .	37	. . . . 5 = 45
	100	121

Concentrated sulphuric acid dissolves the deutoxide of manganese; but the same acid, if much diluted, decomposes it, and forms peroxide, and sulphate of protoxide. The solution acts on metals, an adequate portion of the deutoxide being brought to the state of protoxide. It is also, when heated, decomposed by tartaric acid and binoxalate of potassa, an escape of carbonic acid being in both cases observed. A similar decomposition is produced, by the same agents, of other metallic salts with base of deutoxide.

*Sulphurous acid* acts on the peroxide, first depriving it of part of its oxygen, and becoming sulphuric acid, which dissolves the protoxide.

*Hypo-sulphite of manganese* is obtained by acting on hypo-sulphite of lime with sulphite of manganese.

*Nitrate*.—Nitric acid, when moderately concentrated, dissolves metallic manganese with an escape of nitrous gas. The solution is colourless; but, by long-continued heat, the acid is decomposed, and peroxide is left. The protoxide and white carbonate also dissolve readily in nitric acid, and by particular management crystals may be obtained from the solutions. The crystals deliquesce by exposure to the air; and on the application of heat, melt, and are immediately decomposed, a blackish brown substance remaining, which Berzelius took for the real deutoxide, but which Dr. Forchhammer believes to be a mixture of 1 atom of deutoxide with 1 atom of peroxide. Nitric acid, heated with deutoxide, divides it into protoxide, which is dissolved, and peroxide. The peroxide is not acted upon by nitric acid, unless a little sugar is added, or some other similar substance, which may partly deoxidize it. Crystallized nitrate of manganese consists of

Nitric acid . . . . .	35.	or 1 atom 54
Protoxide of manganese ..	23.5	or 1 atom 36
Water . . . . .	41.5	or 7 atoms 63
	100.	153

*Muriate.*—The action of muriatic acid on the black native oxide is the source of chlorine gas. According to the old theory, part of the acid acts on one portion of the oxide; and first reduces it to the state of protoxide, and then dissolves it; affording muriate of protoxide of manganese. The oxygen, thus liberated, uniting with another portion of muriatic acid, composes oxymuriatic acid. But, on the more probable theory of the simple nature of chlorine, the hydrogen of the muriatic acid is attracted by the oxygen of the oxide, and the chlorine is not formed, but merely set at liberty. (See vol. i. p. 228.)

Muriate of manganese is most easily produced by saturating muriatic acid with the carbonate. It may be obtained, though not easily, in crystals, which are readily soluble in water and alcohol, and consist of

Muriatic acid . . . . .	34	or 1 atom	37
Protoxide of manganese	33	or 1 atom	36
Water . . . . .	34	or 4 atoms	36
	100		109

The muriate of deutoxide can only exist at a temperature below 42° Fahr.; for when its solution is heated, the oxide is resolved into protoxide and peroxide. (Forchhammer.)

Dr. John has investigated the combinations of oxide of manganese with vegetable and metallic acids, the details of which are contained in his paper.

The black oxide of manganese has some properties, which show that it is susceptible of still farther oxidation. It imparts to borate of soda, when melted with it, a violet colour. When this is effected by the blow-pipe, the colour may be destroyed by the interior flame, and again reproduced by the exterior one, or by a small particle of nitre. (Klaproth, i. 243, a.)

#### *Acids of Manganese.*

When black oxide of manganese and nitre, both reduced to powder, are mixed together, and thrown into a red-hot crucible, the nitric acid is decomposed, and we obtain a compound of highly-oxidized manganese with potassa. The same compound may be obtained by fusing together one part of the black oxide, and five or six of solid caustic potassa. It has the singular property of exhibiting different colours, according to the quantity



of water that is added to it. A small quantity gives a green solution; a farther addition changes it to blue; more still to purple; and still larger quantity to a beautiful deep purple.

The experiment may be varied, by putting equal quantities of this substance into two separate glass vessels, and pouring on the one hot, and on the other cold, water. The hot solution has a beautiful green colour, and the cold one is of a deep purple. The same material, with water of different temperatures, assumes various shades of colour. Hence this compound has been termed the *chameleon mineral*. This property is destroyed by a very small quantity of sulphuret of potassa, and by other substances that attract oxygen.

The properties of this singular substance have been investigated by Chevreul, and subsequently by Messrs. Chevillot and Edwards. The latter have ascertained that the colour of the chameleon mineral is owing to manganese, and not to any other metal; that the contact of oxygen gas with the fused materials is essential to its formation, during which oxygen is absorbed; and that the chameleon compound is a neutral salt, susceptible of assuming a regular crystallized form. (Ann. de Chim. et de Phys. iv. 287, and viii. 337.)

When these crystals are heated in contact with hydrogen gas, they cause it to inflame. They detonate violently with phosphorus; and set fire to sulphur, arsenic, and antimony, and indeed to all combustible bodies hitherto tried. The red compound was supposed to be a neutral *manganesiate of potassa*, and the green a *sub-manganesiate*; but it seems more probable, from the experiments of Forchhammer, that the difference between the red and green compounds depends, not on the quantity of potassa combined with the oxide of manganese, but on the proportion of oxygen united with the manganese itself. (Ann. of Philos. xvi. 130.) Conformably with this view, he found that adding alcohol, or carbonate of manganese, to the red compound changed it to green, by abstracting oxygen. The manganese in the latter compound, he considers as forming an acid with a minimum of oxygen; the proportions being 100 metal and 96.847 oxygen, constituting *manganesious acid*; the green salt, therefore, is a *manganesite* of potassa. The red compound contains an acid which may be called the *manganetic*, and its compounds *manganesiates*. In this acid 100 of metal are united with 132 of oxygen, proportions which do not,

any more than those of the manganesious acid, agree with any atomic constitution; the one indicating between 3 and 4, and the other between 4 and 5, atoms of oxygen, to each atom of metal. Though it appears, therefore, that manganese is capable of forming true acids with oxygen, yet the proportion of the elements of these acids may be considered as still undetermined. The probability is, that manganesious acid consists of 1 atom of metal and 3 atoms of oxygen, and the manganesic of 1 atom of base and 4 of oxygen. These proportions, it must be acknowledged, differ very materially from those assigned by Unverdorben, as constituting manganesic acid, *viz.*, 58.74 metal + 41.26 oxygen, or very nearly 28 metal to 20 oxygen, which would make the difference of only half an atom of oxygen between the tritoxide and the manganesic acid. His experiments are not given, however, in sufficient detail (see Phil. Mag. Nov. 1827, p. 393) to enable chemists to judge of the credit to which they are entitled.

*Sulphurets of manganese.*—Manganese, in its metallic state, cannot be brought to combine with *sulphur*. Berthier formed a sulphuret of manganese by heating the proto-sulphate in a charcoal crucible. When thus prepared, it has an iron-grey colour, a semi-metallic lustre, and a crystalline appearance. It consists of 1 atom of metal + 1 atom of sulphur, and its equivalent number is 44. Mr. Dalton procured a similar atomic compound, by precipitating a solution of protoxide with a hydro-sulphuret (sulphureted hydrogen alone not occasioning any precipitation), and heating the precipitate, after being dried, a little below redness. This expelled the water and excess of sulphur. (New System, ii. 162.)

To obtain the proto-sulphuret, Arfwedson fused in a close vessel proto-carbonate of manganese, intimately mixed with twice its weight of sublimed sulphur. To free it from oxide, he fused it a second time with an equal weight of sulphur, augmenting the heat so as to drive off the excess of sulphur. He obtained also a *bi-sulphuret*, by passing sulphureted hydrogen over sulphate of manganese or protoxide of that metal. (Ann. of Phil. N.S. vii. 330.) The native sulphuret, called *mangan-glantz*, he proved also to be a bi-sulphuret.

By passing hydrogen gas over ignited sulphate of manganese perfectly dried, Arfwedson converted it, with a loss of 47.22 per cent. into a compound of an atom of sulphuret with an atom

of protoxide of manganese, or an *oxy-sulphuret*. The colour of this compound is a lighter green than that of the protoxide. It remains unaltered when exposed to the air, and is thus easily distinguished from the protoxide, which speedily absorbs oxygen, and becomes brown. It is also easily distinguished from sulphuret of manganese, which has a much darker green colour, and which, by exposure to air, becomes brown. Its constituents are,

Sulphuret of manganese	55. . . . .	or 1 atom	44
Protoxide of manganese	45. . . . .	or 1 atom	36
			80
100. Weight of its atom			80

*Alloys*.—Manganese unites with most of the *metals*, and composes alloys; none of which are distinguished by important properties.

## SECTION XV.

*Zinc.*

The zinc of commerce, known by the name of *speltre*, is never pure, but contains charcoal, lead, and sulphur. To purify it, zinc must be dissolved in diluted sulphuric acid; a plate of zinc is then to be immersed in the solution, to throw down other metals which it may contain; the solution must be decomposed by subcarbonate of potassa; and the precipitate, after being well washed, ignited with charcoal powder; after which it may be distilled at a white heat, from a stone-ware retort, into a receiver nearly full of water. Even after careful distillation, however, zinc is still liable to contain a small quantity of charcoal.

Zinc is of a brilliant white colour, with a shade of blue. Its specific gravity varies from 6.86 to 7.1, the lightest being the purest. By particular treatment it becomes malleable, and may be beaten into leaves or drawn into wire, as was first announced by Mr. Silvester, in the *Philosophical Magazine*, vol. xxiii. In its ordinary state, zinc may be pulverized when hot, in a heated iron mortar, the pestle being also heated. (Faraday.)

Zinc is melted by a moderate heat, *viz.*, about 680° Fahr., and the fused mass, on cooling, forms regular crystals.

*Oxide of zinc.*—By exposure to the air at a low temperature, zinc slowly acquires a coating of grey oxide; but when kept in a degree of heat, barely sufficient for its fusion, it soon becomes covered with a similar oxide. If thrown into a crucible, or deep earthen pot, heated to whiteness, it suddenly takes fire; burns with a beautiful white flame; and a white and light oxide, mixed with a little carbonate, sublimes, having a considerable resemblance to carded wool. This oxide, however, when once deposited, is no longer volatile; but, if exposed to a violent heat, runs into glass. It has been examined with much attention by Proust, who found it to consist of 80 parts of zinc and 20 oxygen. Gay Lussac (80 Ann. de Chim. 170) and Berzelius (81 Ann. de Ch. 170) have since investigated it, and agree in considering it as composed of

Zinc . . . . .	80.39 . . . . .	100
Oxygen . . . . .	19.61 . . . . .	24.41
	100.	124.41

The atomic weight of zinc, deducible from the composition of the oxide as above stated, is 33; but Dr. Thomson, from the results of his experiments on the synthesis of the oxide (First Princ. i. 52), has been led to conclude that 42 represents its atomic weight, and  $42 - 8 = 34$  that of the metal. This number may be adopted, as it is a mean between the numbers deducible from the experiments of Berzelius and of Brande (Quart. Journ. xiv. 49), the latter of which would make 35 the atomic weight of zinc, and 43 that of the oxide. We may consider then oxide of zinc as composed of

Zinc . . . . .	80.95	.... or 1 atom =	34
Oxygen . . .	19.04	.... or 1 atom =	8
	100.	Weight of its atom	42

By violently heating this oxide in a close vessel, Clément and Desormes long ago found that one half its oxygen was expelled, and Berzelius has since made some observations to show that suboxide of zinc may exist. If so, however, it does not appear to be capable, of serving as a base to acids.

Zinc decomposes water very slowly at common temperatures, requiring, probably, the access of air; but it acts with great rapidity, if the vapour of water be brought into contact with it when ignited. In whatever way it is oxidized, we obtain the compound already described, which is the only known oxide of zinc.

*Chloride of zinc.*—Only one compound of chlorine and zinc is known, called *butter of zinc*. It is obtained by evaporating to dryness the solution of that metal in muriatic acid. The compound is fusible under a dull red heat, and, on cooling, passes through several degrees of consistency, being viscid before it becomes solid. When dissolved in water, a small residue of oxide of zinc is left. From Dr. Davy's analysis, it appears to consist of equal weights of chlorine and zinc; but it is more probably constituted of

Zinc . . . . .	48.57	.... or 1 atom =	34
Chlorine ..	51.43	.... or 1 atom =	36
	100.	Weight of its atom	70

If the application of heat be stopped at the right point, Dr. Thomson finds that a muriate of zinc may be obtained, perfectly

free from water, of which this compound and muriate of ammonia are the only examples. It consists of 1 atom of oxide of zinc 42, and 1 atom of muriatic acid 37, and its atomic weight is 79. (First Princ. ii. 224.)

*Iodine and zinc* unite and form a crystalline compound which is fusible and volatile. It has been investigated by Dr. Thomson (lib. cit. i. 91) and found to consist of

Iodine . . . .	78.48	. . . .	or 1 atom =	124
Zinc . . . .	21.52	. . . .	or 1 atom =	34

100.      Weight of its atom 158

#### *Salts of Zinc.*

*Iodate of zinc* falls down in an insoluble state, when iodate of potassa is added to a solution of sulphate of zinc.

*Hydriodate of zinc.*—By exposure to the air, iodide of zinc attracts moisture, and forms *hydriodate of zinc*. When this salt is mingled with a solution of bi-chloride of mercury, a precipitate is obtained of a beautiful bright scarlet colour.

*Sulphite of zinc* may be obtained by dissolving zinc in sulphurous acid. It is a crystallizable salt, readily soluble in water, but not in alcohol.

*Hypo-sulphite of zinc* is formed by digesting metallic zinc in sulphurous acid. Sulphureted hydrogen gas escapes, and from the solution crystals are obtained by gentle evaporation, which, when dissolved in alcohol, and recrystallized, are the hypo-sulphite.

*Sulphate of zinc.*—Zinc readily dissolves in diluted sulphuric acid, with the exception of a small quantity of black powder, which Vogel found to be composed of charcoal, iron, and sulphate of lead. The acid, during its action on this metal, evolves hydrogen gas; and the gas, when obtained, besides other impurities, holds in suspension a portion of the metal. A stream of it, burned in Cuthbertson's apparatus (pl. iv. fig. 34), has been found, if recently prepared, to occasion the fusion of the platinum wire, though pure hydrogen gas is destitute of this property. This *hydrozincic gas* may also be obtained by a process of Vauquelin. A mixture of the ore of zinc, called blende, or calamine, with charcoal, is to be put into a porcelain tube, which is to be placed horizontally in a furnace, and, when red-hot, the vapour of water is to be driven over it. The gas that is produced, is a mixture of carbonic acid, carbureted hydrogen, and a solution

of zinc in hydrogen gas. The zinc is deposited on the surface of the water, over which this gas is kept; but if burned when recently prepared, the gas exhibits, in consequence of this impregnation, a distinctly blue flame.

The solution of zinc in sulphuric acid, when evaporated to a due degree of density, shoots into regular crystals, the primary form of which is a right rhombic prism. (See Mr. Brooke's fig. Ann. of Phil. N. S. vi. 437.) This salt is soluble in  $2\frac{1}{2}$  parts of cold water; and the zinc is not precipitated by any other metal. If the solution be too much concentrated by evaporation, it deposits, while still hot, an opaque crust on the bottom of the vessel, which is less soluble than the crystals, and is in fact the same as the *white vitriol* of the Germans. (Thomson, First Princ. i. 59, and ii. 353.) Both salts agree in taste, and redden vegetable blues. The crystals formed from a cold solution consist of

Sulphuric acid	27.58	....	or 1 atom =	40
Oxide of zinc .	28.96	....	or 1 atom =	42
Water . . . . .	43.46	....	or 7 atoms =	63
	100.		Weight of its atom	145

The deposit from a hot solution (white vitriol) consists of

Sulphuric acid	36.7	....	or 1 atom =	40
Oxide of zinc .	38.54	....	or 1 atom =	42
Water . . . . .	24.76	....	or 3 atoms =	27
	100.		Weight of its atom	109

*Nitrate of zinc.*—Nitric acid, moderately strong, acts on zinc with great violence. The solution, by evaporation, crystallizes in four-sided prisms, which deliquesce with great rapidity. They consist of 1 atom of acid, 1 of base, and 6 of water.

*Muriate of zinc.*—Muriatic acid, a little diluted, acts on zinc, and evolves hydrogen gas of great purity. The solution is clear, but cannot, by evaporation, be brought to crystallize. When rapidly evaporated, the muriatic solution yields a thick extract, which has somewhat of the viscosity of bird-lime. This, if still more heated, becomes chloride of zinc.

Muriate of zinc in strong solution deposits oxide of zinc on adding water, and on being filtered and further diluted, more oxide separates. Weak solutions, when concentrated by evaporation, dissolve the oxide, which will precipitate again on

dilution. The solution is always slightly acid, and ammonia, when added, does not render it neutral, until all the oxide of zinc is precipitated. (Quart. Journ. vi. 159.)

*Phosphate of zinc* may be obtained either by the direct action of dilute phosphoric acid on zinc, or by decomposing sulphate of zinc with phosphate of soda, which throws down a white powder. When dried in the open air, it is white, tasteless, and does not alter vegetable blues. It consists of 1 atom of base, 1 atom of acid, and 2 atoms of water. Dr. Thomson formed also a *bi-phosphate of zinc*, composed of 1 atom of base, 2 atoms of acid, and 4 atoms of water.

*Carbonate of zinc* is precipitated by carbonate of potassa from sulphate of zinc. After being well washed, and dried in the open air without artificial heat, it consists, according to Thomson, of

Carbonic acid	26.83	....	or 1 atom	=	22
Oxide of zinc	51.22	....	or 1 atom	=	42
Water	21.25	....	or 2 atoms	=	18
	100.		Weight of its atom		82

It is difficult, however, to obtain it with exactly the due proportion of water. If dried at  $212^{\circ}$  it is anhydrous. Carbonate of zinc constitutes, also, the principal part of the mineral called *calamine*, which occurs either anhydrous and crystallized, or amorphous, and most commonly stalactitical, in which state each atom of the carbonate is united with an atom of water.

*Ferro-cyanate of zinc* appears as a yellowish white precipitate on adding ferro-cyanate of potassa to sulphate of zinc.

*Acetate of zinc* may be formed either directly by dissolving the metal or the white oxide in acetic acid, or by mingling the solutions of acetate of lead and sulphate of zinc. An insoluble sulphate of lead is formed, and the acetate of zinc remains in solution. By evaporation it affords a crystallized and beautiful salt.

Zinc is oxidized by being boiled with *pure alkaline solutions*, hydrogen gas is evolved, and a portion of the oxide remains dissolved. A similar compound may be obtained, by projecting a mixture of nitre and zinc filings into a red-hot crucible.

From all the salts of zinc, also, the pure alkalis throw down a *hydrated oxide*, which is soluble in an excess of alkali. The solution by ammonia, when evaporated out of the contact of air, furnishes crystals of a feathery form.



*Zinc and Sulphur.*—Zinc, in its metallic state, would appear to have very little affinity for sulphur, if we were to judge from the difficulty of causing them to unite. A mixture of the white oxide of zinc and flowers of sulphur combines, however, into a yellowish brown mass. Water, impregnated with sulphureted hydrogen, decomposes, after some time, the solutions of zinc, and forms a yellowish white precipitate, which is probably a hydro-sulphuret. Mr. E. Davy, by passing the vapour of sulphur over melted zinc, obtained a white crystalline substance, resembling that natural compound of zinc and sulphur which is called *phosphorescent blende*. Berthier produced an artificial sulphuret by igniting, carefully, purified sulphate of zinc in a charcoal crucible. But, he observes, (Ann. de Chim. et de Phys. xxxiii. 168, n.) that it is apt to contain a little oxide, from which it may be purified by very dilute muriatic acid. When pure it is pulverulent, and as white as the oxide. It consisted of zinc and sulphur in the proportion of 100 to 50, which would give an equivalent number for zinc (32) lower than that derived from the oxide. Dr. Thomson's analysis of the native sulphuret (black blende) gave 32.81 sulphur to 67.19 metal, which are in the proportion of 16 to rather less than 33; and Arfwedson found, in fine transparent crystals of yellow blende, 33.66 sulphur and 66.34 zinc, a proportion agreeing with that of 16 to 31.53. It appears then that a lower equivalent number is derived from the composition of the sulphuret, than from that of the oxide; but this may be owing to the greater difficulty of avoiding sources of error in the analysis of the former compound.

Zinc combines with *phosphorus*. The phosphuret of zinc is of a whitish colour and a metallic lustre, not unlike lead. It has some malleability, exhales a phosphoric smell, and, at a high degree of heat, burns like common zinc.

Zinc is capable of furnishing *alloys* with most of the other metals. Of these the most useful, brass, will be mentioned in treating of copper. It has been lately proposed to apply zinc to the purpose of culinary vessels, pipes for conveying water, sheathing for ships, &c.; but it is rendered unfit for the first object, by the facility with which the weakest acids act upon it; and for the remaining ones, by its eventual though slow oxidation, when long exposed to the operation of air and moisture.

## SECTION XVI.

*Iron.*

Iron has a bluish white colour, and admits of a high degree of polish. It is extremely malleable, though it cannot be beaten out to the same degree of thinness as gold or silver. It is equally ductile, however, with those metals; for it may be drawn out into wire much finer than a human hair; and its tenacity is such that a wire only  $\frac{7.8}{1000}$ ths of an inch in diameter is capable of supporting a weight of nearly 550 lb. Its specific gravity varies from 7.5 to 7.8.

Iron is among the most infusible of the metals. Its melting point is about 158° of Wedgwood. But two pieces of wrought iron, raised to a white heat, become covered with a thin covering of fused metal, and when brought into contact, may be permanently united, or *welded*, by forging. Its chemical properties are the following:

I. *Oxides of Iron.*

*Protoxide.*—When exposed to the atmosphere, especially when the air is moist, iron slowly combines with oxygen, or, in common language, *rusts*. If the temperature of the metal be raised, this change goes on more rapidly; and, when made intensely hot, it takes place with the appearance of actual combustion. The sparks, which are struck from steel by collision with flint, consist of iron in the act of burning; *in vacuo* the sparks cannot be produced, but in oxygen gas they are much more splendid than in common air. (Davy.) The small fragments, too, which fly from a bar of iron during forging, undergo a vivid combustion in the atmosphere; and iron filings, projected upon the blaze of a torch, burn with considerable brilliancy. Iron, also, in bars or in plates, when kept red-hot, becomes covered with a coating of oxide, which separates in scales when the bars are forged with the hammer, or the plates laminated by passing between rollers. The oxide, obtained in these ways, is of a black colour, and is still attracted by the magnet.

The same change is more rapidly produced, when ignited iron is brought into contact with oxygen gas; for a vivid combustion then takes place. Lavoisier made many experiments to ascertain the increase of weight, acquired by iron when thus burned, and concluded that, on an average, 100 parts of iron

acquire from 32 to 35 parts of oxygen. Dr. Thomson, however, on repeating the experiment several times, did not find that 100 parts of iron absorbed more than 27.5 of oxygen; but he acknowledges that it is almost impossible to collect the whole product, and that minute portions are dissipated in sparks. (27 Nich. Jour. 381.)

By contact with water at the temperature of the atmosphere, iron becomes slowly oxidized, and hydrogen gas is evolved. It has been observed by Dr. Marshall Hall (Quart. Journ. vii. 55) that water, provided it be entirely deprived of oxygen gas, and secured from contact with atmospheric air, does not oxidate iron at common temperatures; and that a polished plate of iron retains its metallic brilliancy, both in air deprived of moisture, and in water thoroughly purged of air. M. Guibourt, however, has shown that this inaction of pure water on iron takes place, only when the quantity of metal relatively to the fluid is very small; that at 75° to 80° Fahr. little or no effect is produced; but that a temperature of from 120° to 140° Fahr. renders water decomposable by iron, especially when the metal bears a considerable proportion to the water. (Ann. de Chim. et de Phys. xi. 40.) To decide this question, Dr. Hall has recently had recourse to fresh experiments, which have satisfied him that the apparent action of iron on water is due to the presence of carbonic acid; and that, if this be removed by long boiling, or by adding to the water some substance (lime or magnesia for instance) that combines with the carbonic acid, the decomposition of water is entirely arrested. (Quart. Journ. N.S. iii. 262.)

When the steam of water is brought into contact with red-hot iron, the iron is converted into the black oxide; and an immense quantity of hydrogen gas is set at liberty, and may be collected by a proper apparatus. Iron thus treated, though still magnetic, is found to have lost all its tenacity, and may be crumbled down into a black powder, to which the name of *finery cinder* was given by Dr. Priestley. In composition, it differs from the oxide of iron obtained by the action of atmospheric air, and probably contains water, or a little peroxide; for 28 parts of iron were found by Priestley to have gained rather more than 9.5 in weight; and Gay Lussac observed an increase of 37.8 on 100 iron, over which steam had been passed at a red heat. By a careful repetition of the process, Dr. Thomson, however, found that 100 grains of iron, ignited in contact with the vapour of water, acquire 29.1 grains of oxygen. The fixa-

tion of oxygen by iron thus treated appears then to be varied by some unexplained circumstance.

When iron is dissolved in diluted sulphuric acid, the acid is not decomposed; but the metal is oxidized at the expense of the water, and hydrogen gas is obtained in abundance. Now as water is composed of two volumes of hydrogen and one of oxygen, a quantity of oxygen, equal in volume to half the hydrogen gas obtained, must have combined with the metal; that is, for every 200 cubic inches of hydrogen, oxygen equal to 100 cubic inches or = 33.8 grains, must have united with the metal. But 100 grains of pure iron evolve, by acting on dilute sulphuric acid, 170 cubic inches of hydrogen gas at a mean of the barometer and thermometer, showing that oxygen, = 85 cubic inches, or 28.73 grains, must have united with the metal, during its solution. Dr. Thomson, from an experiment of this kind, found that 35 grains of iron, after the action of dilute sulphuric acid, had gained 10 grs. of oxygen, 59 cubic inches of hydrogen being evolved. It is to be considered, however, that the purity of the iron employed will materially affect the result; for if the iron contain charcoal, as is almost always the case, a little carbureted hydrogen gas will be mixed with the hydrogen; and the hydrogen in that gas being in a condensed state, the apparent will be less than the real quantity of hydrogen disengaged. Perfect accuracy would require, also, that allowance should be made for the aqueous vapour mixed with the hydrogen gas.

Iron, by the last process which has been described, is converted into an oxide of a black colour, still retaining the magnetic property. Its composition has been the subject of a series of experiments by Bucholz, who concludes that 100 parts of iron, to become the black protoxide, condense 29.83 parts of oxygen; Dr. Wollaston deduces the oxygen to be 29 parts, Berzelius 29.5, and Dobereiner makes it 30. The equivalent number for iron will, of course, vary, accordingly as we adopt one or other of these experimental results. If 29.5 be admitted to be the quantity of oxygen which converts 100 of iron into protoxide, the equivalent of that metal will be 27; if 28.5, the equivalent of iron will be 28; and we may adopt 28 for the atomic weight of iron, because it agrees with the best analyses of its salts and other compounds. That of the protoxide then will be  $28 + 8 = 36$ .

*Peroxide.*—When the protoxide of iron, or iron itself, is dissolved in nitric acid; then boiled for some time; and, after being precipitated by ammonia, is washed, dried, and calcined in a low red heat, it is found to be converted into a brownish red oxide, which is not at all magnetic. It forms salts generally of a red colour, the solutions of which are precipitated of a fine blue by ferro-cyanate of potassa, and of an intense bluish black by infusion of galls. The peroxide of iron is reconverted into the protoxide by passing dry hydrogen gas over it, when heated to a little below redness. By this process, first practised by Stromeyer, the protoxide may be obtained pure. In this state, it is exceedingly combustible, and catches fire when exposed to air at common temperatures; being again converted back into peroxide.

*Peroxide of iron*, according to Bucholz, is composed of 100 parts of iron and 42 of oxygen; to Dobereiner, of 100 iron and 45 oxygen; to Berzelius, of 100 iron and 44.25 oxygen, or, according to Dr. Wollaston, of 100 metal and 43.5 oxygen. If the oxygen in the peroxide be a multiple by  $1\frac{1}{2}$  of that in the protoxide, the peroxide should consist of 28 metal + 12 of oxygen, and its equivalent number should be 40; and 100 metal should be united with 42.75 of oxygen. We have therefore two well-characterized oxides of iron:

	Iron.	Oxygen.	Atomic Wt.
1. The protoxide . . . .	28 . . . . .	8 . . . . .	36
2. The peroxide . . . .	28 . . . . .	12 . . . . .	40

Beside these, it has been attempted to be shown that there are other oxides of iron. Thenard contends for a compound, containing less oxygen than the black oxide, *viz.*, 25 parts to 100 metal; a second composed of 37.5 oxygen to 100 metal; and a third of 50 to 100 metal. And Gay Lussac, also, supports the notion of three oxides, with proportions, however, differing from those of Thenard. The first oxide he obtained by dissolving iron in diluted sulphuric or muriatic acid, out of the contact of air. It is precipitated white by alkalis, and by ferro-prussiates, and is composed of 100 iron and 28.3 oxygen, it is therefore identical with the protoxide. The second, or deutoxide, is obtained when iron is oxidized by the vapour of water or by oxygen gas, and consists of 100 iron and 37.8 oxygen. This he supposes to constitute the octohedral and magnetic iron ores. The third is the acknowledged red oxide, which is composed of

100 iron and 42.31 oxygen. (80 Ann. de Chim. 163, and 1 Ann. de Chim. et Phys. 33.) It is ascertained, however, that the only oxides, capable of forming distinct neutral salts with acids, are the two, the composition of which has already been stated on the authority of Bucholz, Wollaston, and Berzelius; and that the new oxide of Gay Lussac is a compound of the protoxide and peroxide in atomic proportions, *viz.*,

	Iron.	Oxygen.	Atom. Wt.
1 atom of protoxide . . . . .	28	8	36
2 atoms of peroxide . . . . .	56	24	80
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	84	32	116

And 84 : 32 :: 100 : 38, which agrees very nearly with experiment.

Again, the scales, detached by hammering or rolling, from bars or plates of iron, which have been strongly heated, were found by Berthier to consist of

Protoxide of iron ..	64 or 2 atoms =	72
Peroxide . . . . .	36 or 1 atom =	40
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100	112

Mosander, however, has shown that the composition of these scales is by no means homogeneous; and that, apart from impurities, the exterior layer is constituted as represented by Berthier, while the interior one consists of 3 atoms protoxide + 1 atom peroxide. (Ann. de Ch. et de Ph. xxxiv. 168.)

It may be remarked, on comparing the composition of the two oxides of iron, that the oxygen of the protoxide is not a multiple of that of the peroxide by an entire, but by a fractional number, *viz.*, 1.5. This anomaly has already been shown to be reconcileable with the principles of the atomic system (vol. i. p. 50).

There appear to be two *hydrates* or *hydro-oxides*, corresponding to the two oxides of iron, which are obtained whenever we precipitate their respective solutions in an acid, by a fixed alkali. The hydrate of the protoxide is white, with a tinge of olive or green; that of the peroxide is orange coloured. The former hydrate passes to the latter, by exposure to the atmosphere. Ochre, it has been shown by Leidbeck, is a native hydrate of the peroxide, mechanically mixed with earthy ingredients; but, exclusively of them, composed of from 60 to 62 peroxide of iron

and 20.2 to 25 water. (80 Ann. de Chim. 163.) The proportions indicating two atoms of water to one of peroxide would be 62 parts by weight of the latter to 26.4 of the former, numbers not very remote from those obtained by experiment. The preparation of a pure hydrate of iron was found by Berzelius to be attended with great difficulty, on account of the readiness with which it parts with water. The ore of iron, called *brown hæmatite*, is a native hydroxide, consisting of 1 atom of peroxide + 1 atom of water. The *red hæmatite* appears to be the peroxide uncombined with water.

## II. Chlorides of Iron.

*Chlorine* combines with iron in two proportions. When iron is dissolved in diluted muriatic acid, a green solution is obtained, which may be evaporated to dryness out of the contact of air, and nearly ignited with similar caution. The product is a grey brittle lamellated substance, which, when analyzed by Dr. Davy, was found to consist of

Chlorine	.....	53.2	.....	100	.....	113.63
Iron	.....	46.8	.....	88	.....	100.

100.

If constituted, as there can be little doubt that it is, of 1 atom of chlorine = 36, + 1 atom of base = 28, its composition ought to be

Chlorine	....	56.3	.....	100.	.....	128.85
Iron	.....	43.7	.....	77.6	.....	100.

100.

When iron wire is burned in chlorine gas, a substance of a bright yellowish brown colour is formed, with a high degree of lustre; volatile at a temperature a little above  $212^{\circ}$ , and crystallizing in small iridescent plates. It acts violently on water, and gives a red solution. It consists of

Chlorine	.....	66.1	.....	100.	....	194.174
Iron	.....	33.9	.....	51.5	....	100.

100.

In this case, as in that of peroxide of iron, we have the apparent anomaly of an atom and a half of chlorine being united with an atom of iron; for  $100 : 51.5 :: 36 \times 1\frac{1}{2} = 54 : 28$ .

*Chloride of iron* has not been much examined.

*Iodine and iron* unite and form a brown fusible compound, which decomposes water, and passes to the state of a green hydriodate of iron.

*Iodate of iron* is not accurately known.

### III. *Salts of Iron.*

1. *Proto-sulphate of iron.*—When diluted sulphuric acid is made to act on iron, we obtain a compound of that acid with the protoxide. The solution, evaporated out of the contact of air, yields crystals, which have a beautiful green colour, and the shape of oblique rhombic prisms, not of rhomboids, as is sometimes represented (Brooke, Ann. Phil. N.S. vi. 120). They have a strong styptic taste; redden vegetable blue colours; and are soluble in about two parts of cold and  $\frac{3}{4}$ ths their weight of boiling water. The solution is precipitated of a greenish white by alkalis, and white by prussiate of potassa, but is not changed by infusion of galls, so long as air is excluded. It absorbs oxygen from the air, and the metal passes to the state of peroxide; it also absorbs nitrous gas; and is converted, by chlorine and its compounds, into a sulphate of peroxide. When the crystals are moderately heated, 100 parts lose 40 of water, and the residue consists of 1 atom of sulphate + 1 atom of water. This residue, distilled at a stronger heat, is decomposed, and yields a strong fuming acid, called *glacial sulphuric acid*. The proto-sulphate is composed, according to Berzelius, of

		Atoms.	
Sulphuric acid . . . . .	28.9	1 =	40
Protoxide of iron . . . . .	25.7	1 =	36
Water . . . . .	45.4	7 =	63
	100.		139

Crystals of proto-sulphate of iron are also deprived of most of their water by concentrated sulphuric acid, and when drained may be applied to the production of fuming sulphuric acid. (Bussy, Ann. de Ch. et de Ph. xxx. 20.)

When a solution of proto-sulphate of iron is heated with access of air, part of the protoxide passes to the state of peroxide, and, combining with a portion of acid, falls down in the form of a yellow powder, which, according to Berzelius, is a sulphate of the peroxide with *excess of base*, or a *sub-persulphate*. The proportions of its components are :



		Atoms.
Sulphuric acid	15.5	1 = 40
Peroxide of iron	63.	4 = 160
Water	21.5	6 = 54
	100.	254

Other sulphates with base of peroxide of iron (called, from the atomic proportions of their constituents, *per-bisulphate*, and *per-quadrissulphate*), have been investigated by Dr. Thomson,\* Mr. Sylvester,† and Mr. Cooper,‡ but no sulphate of protoxide with *excess* of acid is yet known.

The farther oxidation of the iron in the green sulphate is effected more expeditiously by boiling its solution with nitric acid, and evaporating to dryness, care being taken not to raise the heat so as to expel the sulphuric acid. Water, added to the residuum, dissolves a salt, which is composed of sulphuric acid and peroxide. The solution has a yellowish colour; does not afford crystals; but, when evaporated to dryness, forms a deliquescent mass, which is soluble in alcohol, and may thus be separated from the green sulphate. Its solution affords a blue precipitate with ferro-prussiate of potassa. This salt has been called *per-sesquisulphate of iron*. It consists, according to Berzelius, of

		Atoms.
Sulphuric acid	60.44	100. .. 1½ = 60
Peroxide of iron	39.56	65.5 .. 1 = 40
	100.	165.5      100

The *sulphurous acid*, also, unites with protoxide of iron, and forms a sulphite; and this sulphite, taking an additional quantity of sulphur, composes a sulphureted sulphite. The precise composition of these salts remains to be determined.

The *Nitrate of iron*, it was long ago shown by Sir H. Davy, may exist in two different states, the green or proto-nitrate, in which the oxide is at the minimum of oxidation, and the red, in which it is at the maximum.

To obtain nitrate of iron, in which the oxide is at the minimum, acid of the specific gravity of 1.25, or even less, must be used; the iron must be added in large pieces, and at distant intervals; and the operation carried on without the access of

\* Ann. of Phil. x. 102.

† Ib. xiii. 466.

‡ Ib. 298.

air. When this solution is made on a large scale for the purposes of the dyer, it is proper to connect the vessel, in which it is prepared, with a large receiver; for, in the latter, a quantity of nitrous acid will be found, which is worth the trouble of collecting. If confined in a vacuum along with sulphuric acid, it yields light green rhomboidal prisms, which Dr. Thomson regards as constituted of 1 atom of acid, 1 of base, and 7 of water.

Nitrate of iron, thus prepared, passes, on exposure to the atmosphere, to the state of that in which the oxide is at the maximum; or we may obtain the per-nitrate by leaving nitric acid for a long time in contact with protoxide of iron. Crystals form spontaneously in the liquid, which are at first transparent and colourless, but become brown by keeping; their taste is acid and astringent, and they redden vegetable blues. They contain per cent. 18 base, 41 acid, and 41 water, proportions which agree best with those of a *per-sesquinitrate*.

*Muriate of Iron.*—Muriatic acid moderately diluted dissolves iron and its oxides with great ease; and affords two distinct salts, differing from each other according to the state of oxidation of the metal. The muriate containing the black oxide is green, and that containing the oxide at the maximum, red. The proto-muriate resembles the proto-sulphate in the colour of its crystals. These have the form of rhombic plates, and are soluble both in water and in alcohol. They consist, according to Dr. Thomson, of 1 atom of muriatic acid, 1 atom of protoxide of iron, and 3 atoms of water.

The green muriate is convertible into the red by simple exposure to the atmosphere. Berzelius describes a striking experiment founded on this property. If a solution of the green muriate be exposed to the atmosphere, in a tall cylindrical glass jar, for some days, and a few drops of pure ammonia be then introduced at different depths by means of a tube, the precipitate formed near the surface will be green; a little lower, blue; still lower, greyish; then of a dirty white; and at the bottom perfectly white, provided time has not been allowed for the atmospheric oxygen to penetrate so low. It is remarkable that the addition of sugar or of tartaric acid, but not of gum, though in composition very nearly allied to sugar, to the permuriate of iron, prevents ammonia from exerting its usual action as a precipitant. (Quart. Journ. xxi. 394.)

*Phosphate of iron.*—Phosphoric acid acts with but little

energy on iron; but both the oxides of iron may be made to combine with phosphoric acid by double affinity. From the mixed solutions of proto-sulphate of iron and phosphate of soda, a pale blue precipitate is formed. It is soluble in most acids, and precipitated again by ammonia without change. The proto-phosphate of iron is found also native, both in the state of a powder and of fine blue crystals. It consists of 1 atom of protoxide, and 1 atom of acid, with various proportions of water.

The *per-phosphate* is formed by mingling the solutions of per-sulphate of iron and phosphate of soda, when an insoluble yellowish white precipitate results.

*Carbonate of iron.*—The only oxide of iron, so far as is yet known, that is capable of uniting with carbonic acid, is the protoxide. Proto-carbonate of iron is found native, consisting of 1 atom of protoxide + 1 atom of carbonic acid. It has not been formed artificially; nor are we acquainted with any solid compound of the peroxide of iron with carbonic acid. The sub-carbonate of the London Pharmacopœia is composed of about 40 per cent. carbonate of iron, and 60 of the peroxide. (Phillips.)

*Ferro-cyanate of iron, or prussian blue.*—The process for preparing *prussian blue* consists in calcining together, in a covered crucible, equal weights of dried blood, horn shavings, or almost any animal substance, and carbonate of potassa; then lixiviating the product, which is a cyanide of potassium; and mixing the liquid (called formerly *lixivium sanguinis*) with a solution of two parts of alum and one of proto-sulphate of iron. The precipitate, which has a dingy green colour, is to be washed first with muriatic acid, which changes it to a beautiful deep blue, and then with abundance of water. The process, however, of which this is a mere outline, is one of some nicety, and requires attention to a number of minute observances, for the details of which I refer to Martyn's Abridgment of the Philosophical Transactions, vol. vii. p. 747.

Though prussian blue was discovered so long ago as the year 1710, yet its nature was not understood till Scheele, in 1782, rendered it the subject of an excellent essay, published in the collection of the Royal Academy of Stockholm, and also in his works. (Essay 20, 21.) It had, previously to that time, been examined by Macquer, and has since been ably investigated by Berthollet, Proust, Vauquelin, Porrett, Thomson, Gay Lussac, Robiquet, and Berzelius; but still, it appears, without

our having attained that certainty about its composition, which we have acquired respecting the generality of chemical compounds.

The prussian blue of commerce is an impure substance, and contains a variety of other matters, especially a quantity of alumine. For chemical experiments, it is proper, therefore, to prepare it by mixing the solutions of ferro-cyanate of potassa and proto-sulphate or proto-muriate of iron, and washing the precipitate, first with muriatic acid, and then with water. The precipitate produced is at first an exceedingly light blue, and continues so, as long as it is guarded from the action of the atmosphere; but it changes to a deeper blue by exposure to the air, or by mixture with any agent capable of imparting oxygen. If persulphate of iron be substituted for the proto-sulphate, the precipitate is at first apparently of a fine colour, but becomes, by drying, almost black. From the necessity which exists of using the proto-salt, in order to obtain a fine pigment, Dr. Thomson is disposed to believe that the iron is in the state of Gay Lussac's oxide, but admits that this would be the only instance of its forming a distinct combination.

Prussian blue is insoluble in water, and in acids, unless when they are concentrated and heated. When thoroughly dried, it shows a great affinity for moisture, by absorbing it rapidly from the atmosphere. It is not decomposed by being heated to 307° Fahr.; but, at a higher temperature, it catches fire, and burns in the manner of tinder, leaving from 54 to 60 per cent. of oxide of iron.

When prussian blue in fine powder is added to a heated solution of potassa, a hydrated peroxide of iron is separated, the colour of which is not a bad indicator of the value of the pigment used in the arts; for its excellence bears a proportion to the deep redness of the oxide. The liquor is a solution of the salt, which has already been described as the *ferro-cyanate of potassa*.

When prussian blue is kept in contact with water and iron filings, or with sulphureted hydrogen, it is decomposed, in consequence of the de-oxidation of the iron, and reduced to the state of the white compound; but this again becomes blue on restoring oxygen.

Pure prussian blue, added to concentrated sulphuric acid, increases in volume, and becomes white; but its colour is

restored by adding a sufficiency of water. Muriatic acid has no action on it, unless when concentrated and heated, and then (as Robiquet has shown, *Ann. de Ch. et de Phys.* xii. 284) it separates the greater part of the oxide of iron, leaving a crystallizable substance, analogous to that which is obtained by decomposing ferro-cyanate of potassa by tartaric acid, and which Mr. Porrett has termed *ferrureted chyazic acid*.

Beside prussian blue, there appears, from Berzelius's experiments (*Ann. of Phil. N.S.* i. 444), to be another blue compound of the same elements, which is soluble to some extent in water. Prussian blue, in the dingy green state in which it is first precipitated by *livivium sanguinis*, seems also to contain an excess of base, which muriatic acid removes. There are probably, therefore, three compounds in which the peroxide, and one in which the protoxide, exists as the base.

Prussian blue, submitted to distillation *per se*, gives water, hydro-cyanate of ammonia, carbonic acid, and other gases.

Respecting the nature of prussian blue, a variety of opinions have been entertained, and it is still a subject on which chemists are by no means agreed. No theory respecting it can be entitled to notice that was anterior to Gay Lussac's important discovery of cyanogen. His researches led him to believe that prussian blue is a compound of cyanogen with metallic iron, and that it is, therefore, not a prussiate, but a *cyanide*; but Vauquelin, having directed his attention to this part of the subject, was still induced to regard it as a true prussiate. According to Mr. Porrett's view, it is a compound of ferro-cyanic acid with peroxide of iron. Berzelius, not admitting the existence of any such acid as the ferro-cyanic, regards prussian blue as a compound of hydro-cyanate of protoxide of iron with peroxide of iron, in proportions admitting of some variation. (*Ann. of Phil. N.S.* i. 444.) Robiquet, on the other hand, considers it as a cyanide of iron, combined with a ferro-cyanate of the peroxide and with water. (*Ann. de Chim. et Phys.* xii. and xvii.) The subject, in its present state, appears to me very obscure, and I refer the reader, who is disposed to examine it, to the papers of Berzelius and Robiquet already quoted. (See also vol. i. p. 573.)

*Tanno-gallate of iron*.—When sulphate of iron is mixed with an infusion of galls, we obtain a black solution, which is a new combination of oxide of iron with the gallic acid and tan.

Both the gallate and tannate of iron are essential constituents of writing inks, the other ingredients of which are chiefly added with the view of keeping these insoluble compounds suspended.

In order that the iron may unite with the gallic acid and tan, it must exist in combination with the sulphuric acid in the state of red oxide; for the protoxide does not form a black compound with these substances. Iron filings, however, dissolve in an infusion of galls, with an extrication of hydrogen gas; but the compound is not black till after exposure to air, which oxidizes the iron still farther. This solution, with a sufficient quantity of gum, forms an excellent writing ink.

On the same principle may be explained the effect of metallic iron in destroying the colour of ink. When ink is digested with iron filings, and frequently shaken, its colour decays; and it also becomes colourless after having a stream of sulphureted hydrogen gas passed through it. In both these cases, the oxide of iron is partly deoxidized. Characters written with ink, after this treatment, are at first illegible, but become black as the iron acquires oxygen again from the air.

The combination of iron, forming ink, is destroyed by pure and carbonated alkalis. Apply a solution of alkali to characters written with common ink, the blackness will disappear, and the characters will become brown, an oxide of iron only remaining on the paper. Alkalis, added cautiously to liquid ink, precipitate the black combination, but an excess of alkali redissolves the precipitate.

Characters, which have been effaced by alkalis, may again be rendered legible by an infusion of galls.

Ink is also decomposed by most acids, which separate the oxide of iron from the gallic acid, in consequence of a stronger affinity. Hence ink-stains are removed by dilute muriatic acid, and by some vegetable acids. Hence, also, if to a saturated solution of sulphate of iron there be added an excess of acid, the precipitate no longer appears on adding infusion of galls. When a mixture of ink with nitric acid is heated, the yellow oxalate of iron is formed, and is precipitated on adding pure ammonia.

Ink is decomposed by age, partly in consequence of the farther oxidation of the iron, and partly, perhaps, in consequence of the destruction of the acid of galls. Hence ink-stains degenerate into iron-moulds, and these last are immediately produced

on an inked spot of linen when washed with soap, because the alkali of the soap abstracts the gallic acid, and leaves only an oxide of iron. Ink is decomposed also by chlorine, which destroys the gallic acid, and the resulting muriatic acid dissolves the oxide of iron.

*Succinate of iron.*—The succinic acid composes with peroxide of iron a brown mass, insoluble in water. The combination is best effected by double decomposition, and especially by the addition of a solution of succinate of ammonia to any persalt of iron. A brown red precipitate of succinate of iron falls down. This precipitate Klaproth exposed to heat, first by itself, and afterwards mixed with a small quantity of linseed oil. The first operation destroys the acid, and the second reduces the metal to the state of black oxide. Now as the black oxide contains, in 100 parts, 77.2 of metallic iron, the precipitation of a solution, by succinate of ammonia, affords a ready method of estimating the quantity of iron in any solution of that metal, or in any of its salts.

*Acetate of iron.*—The acetic acid, or even common vinegar, acts slowly upon iron, and forms a solution, which is of great use in dyeing and calico-printing. The acetate of iron may also be obtained by double decomposition, if we mingle the solutions of acetate of lime or of lead with one of sulphate of iron. It may be formed, also, by boiling acetate of lead with metallic iron, which precipitates the lead in a metallic state. This combination of iron with acetous acid may exist, like its other salts, in two different states. In the one, the oxide is at the minimum, and in the other at the maximum of oxidation. It is the latter salt chiefly which is adapted to the use of the dyer and calico-printer.

*Silicate of iron.*—This compound may be obtained by mixing the solutions of silicate of soda and permuriate of iron. (Walcker, in Quart. Journ. N.S. iii. 372.)

*Sulphuret of iron.*—Iron combines with sulphur, and affords compounds, the characters of which vary according to the proportions of their components. (a) A paste of iron filings, sulphur, and water, if in sufficient quantity, will burst, after some time, into flame. (b) A mixture of one part of iron filings and three parts of sulphur, accurately mixed, and melted in a glass tube, at the moment of union exhibits a brilliant combustion. The best method, however, of effecting the combination

of iron and sulphur, is to take a bar of the metal, while of a glowing heat, from a smith's forge, and to rub it with a roll of sulphur. The compound of iron and sulphur falls down in drops, and may be preserved in a phial. Of the compounds of sulphur, this is one of those which are best adapted for affording pure sulphureted hydrogen gas with diluted acids. (c) Berthier formed the proto-sulphuret of iron by heating the proto-sulphate in a charcoal crucible. (d) It may be obtained by adding a hydro-sulphuret to a solution of the protoxide of iron in any acid.

In the sulphuret, made artificially by fusion, as well as in the native sulphuret, iron (it has been shown by Proust and Mr. Hatchett) is in the metallic state. Two compounds of iron and sulphur have been proved to exist, the one with a smaller, the other with a larger proportion of sulphur. The former, which is distinguished by the property of being magnetic, is the *proto-sulphuret*. The *bi-sulphuret* is known only as a natural product; it is not magnetic; is nearly insoluble in diluted sulphuric and muriatic acids; and gives no sulphureted hydrogen gas. The proto-sulphuret, on the other hand, is readily soluble in dilute acids, and gives during solution abundance of sulphureted hydrogen; but nitric acid oxygenates the sulphur, and oxidizes the metal. It is decomposed when fused with alkaline carbonates. It consists of

		Atoms.	
Iron . . . . .	63.64 . . . .	100. . . . .	. . . . 1 = 28
Sulphur . . . . .	36.36 . . . .	57.14 . . . .	. . . . 1 = 16
	100.		44

And the bi-sulphuret is composed of

Iron . . . . .	46.73 . . . .	100. . . . .	. . . . 1 = 28
Sulphur . . . . .	53.27 . . . .	114.28 . . . .	. . . . 2 = 32
	100.		60

The artificial sulphuret varies in its composition, owing probably to the sulphuret being mixed with different proportions of metallic iron. The foregoing appear to be the only well ascertained and definite compounds of iron and sulphur. Gay Lussac, however, contends for three sulphurets corresponding to his supposed three oxides of iron (80 Ann. de Ch. 170); and Dr. Thomson describes a *sesqui-sulphuret*, constituted of 28 parts iron and 24 sulphur, which is obtained by pouring a solu-



tion of neutral persulphate of iron into hydrosulphuret of potassa. (First Princ. ii. 191.) Mr. Dalton describes a compound of 1 atom of iron with 5 atoms of sulphur, produced by mixing a solution of proto-sulphate of iron with a due proportion of quadri-sulphuret of lime. (New System, ii. 136.) Arfwedson, also, has added two to the number of sulphurets; one, which he prepared by passing hydrogen gas over ignited sulphate of iron, and another, resulting from a similar treatment of the subpersulphate. (Ann. of Phil. N.S. vii. 341.) But all these compounds require to be further examined, before we can admit them to be distinct atomic combinations.

*Carburet of iron.*—Iron combines with carbon in various proportions, which occasion great differences of properties in the compounds. On these varieties, and the occasional combination of a small proportion of oxygen, depend the qualities of the different kinds of iron used in the arts, as cast iron, steel, &c. &c. The quantity of carbon, in the sub-carburets of iron, may be determined by solution in sulphurous acid, which dissolves the iron and sulphur, and has no action on carbon. An ingenious mode of analysis, employed by Mr. Mushet, consists in ascertaining the quantity of litharge, which a given quantity of the iron under examination is capable of reducing, by fusion, to a metallic state.

There can scarcely be a more striking example of essential differences in external and physical characters being produced by slight differences of chemical composition, than in the carburets of iron; for steel owes its properties to not more than from  $\frac{1}{60}$ th to  $\frac{1}{140}$ th its weight of carbon. This appears to be the only addition necessary to convert iron into steel; for though it is proved that the best steel is made from iron which has been procured from ores containing manganese, yet careful and skilful analysis discovers no manganese in steel. (Ann. de Chim. et de Phys. iii.)

*Cast or crude iron*, besides other casual impurities, contains oxygen, carbon, phosphorus, and the base of silica. Its differences depend chiefly on the various proportions of carbon, which is greatest in the black, and least in the grey, variety of iron. Berzelius, indeed, denies the presence of oxygen in cast iron, and asserts that its differences of quality are produced by variable proportions of charcoal, manganese, and the bases of magnesia, lime, and silica. (40 Phil. Mag. p. 245.) By the

process of refining, or *puddling*, as it is called, which is well described by Dr. Beddoes in the 81st vol. of the Philosophical Transactions, *cast* is converted into *malleable* iron; the carbon and oxygen unite together, and escape in the form of carbonic oxide; while another part of the oxide of iron unites to the earthy matter, and rises to the surface in the form of a dense slag. A large quantity of impurities is afterwards mechanically squeezed out, by passing the bars of iron between rollers. After this process, it forms *malleable* or *bar iron*, which, though the purest form of iron of commerce, may be considered as iron still holding some oxygen and carbon in combination, the latter of which, even in very ductile iron, amounts, according to Berzelius, to about one-half per cent. Hassenfratz has suggested that iron, which has been manufactured with wood charcoal, may probably contain potassium, and may owe its superiority to this circumstance; and Berzelius has rendered it probable that even the most ductile iron may contain silicium. (78 Ann. de Chim. p. 233.)

If bar iron be long and slowly heated, in contact with charcoal, or if it be exposed ignited to a current of carbureted hydrogen gas, as in Mr. Macintosh's process, it loses oxygen and acquires carbon, and thus becomes converted into *steel*. *Steel of cementation* is made by stratifying bars of pure iron with charcoal powder in large earthen crucibles, carefully closed with clay. These are exposed to a high degree of heat in a furnace, during eight or ten days. This, from the appearance of blisters on its surface, is called *blistered steel*. (Collier on the Manufacture of Steel, Manchester Soc. Mem. vol. v.) A small proportion only of carbon, united with iron, is not capable of depriving it entirely of the properties of malleable iron; for though it becomes a good deal harder, yet it may still be welded. By union with a still farther quantity of carbon, it loses altogether the property of welding; is rendered harder and more compact; and, after being melted in a crucible with pounded glass and charcoal, forms the fine *cast steel*. Steel, therefore, though like cast iron it contains carbon, yet differs from it essentially in being destitute of oxygen and earthy matter. The charcoal which it contains may be exhibited in the form of a black stain, on applying a drop of almost any weak acid to the surface of polished steel.

Steel, when ignited and suddenly cooled, is rendered so hard

and brittle, as to be unfit for any useful purpose. To remove this defect, it requires what is called *tempering*, which consists in heating it up to a point that varies with the object to which the steel is destined. When thus heated, it assumes various colours, which were formerly the only guide for judging of the degree of temper; but this is now much better ascertained by using a bath of mercury or fusible metal, and regulating its temperature by the thermometer, which may range from 400° to 600° Fahr. according to the use for which the steel is intended.

Steel admits of being alloyed with several other metals, and the alloys, as appears from the investigation of Messrs. Stodart and Faraday (Phil. Trans. 1822), are applicable to various important uses. The silver alloy, containing about  $\frac{1}{500}$  of that metal, may be advantageously applied to every purpose for which good steel is required. With  $\frac{1}{100}$  of platinum, steel acquired such an increase of toughness as well as of hardness, as fully to compensate its additional cost. With rhodium, as well as with iridium and osmium, very valuable compounds were obtained; but till these metals can be had at less cost and in greater quantity, their compounds with steel can be of little practical use, except for small and delicate instruments. In the analysis of these alloys, Mr. Faraday remarked that some of them, especially that into which platinum entered in the proportion of not more than  $\frac{1}{100}$ th, was acted on with great energy by dilute sulphuric acid, gas being evolved very rapidly, and the alloy dissolved in a time during which pure steel was scarcely affected. This effect he ascribes to the formation of a Voltaic combination by the two metals. It could not be owing to the mere separation of the particles of steel by the interposed foreign metal; for the effect was diminished by increasing the proportion of platinum.

The theory of the production of steel, which was long generally received, was that it is a compound of iron and carbon, or a carburet of iron; but, if so, the latter element must be in very small proportion, for the iron gains not more than  $\frac{1}{80}$  of its weight by conversion into steel. Pure steel, Mr. Dalton asserts (New Syst. ii. 217), dissolves without residuum in acids, and that the hydrogen evolved by diluted sulphuric acid is free from carbon. He is disposed, therefore, to believe, that the properties distinguishing steel from iron are rather owing to a peculiar

crystallization, or new arrangement of the particles of iron, than to their combination with any other substance.

Another combination of iron and carbon, which is a true carburet of iron, is the substance called *plumbago*, *graphite*, or black-lead, used in fabricating pencils, and in covering iron to prevent rust. By exposure to the combined action of heat and air, the carbon is burned off, and protoxide of iron remains. When mingled, also, with powdered nitrate of potassa, and thrown into a crucible, a deflagration ensues; and peroxide of iron may be obtained by washing off the alkali of the nitre. From the experiments of Messrs. Allen and Pepys, it appears that pure plumbago, when burnt in oxygen gas, leaves a residue of oxide of iron amounting only to about 5 per cent.; and that it gives very nearly the same quantity of carbonic acid, by combustion, as the diamond and charcoal. When intensely heated in a Toricellian vacuum by a Voltaic battery, Sir H. Davy found that its characters remained wholly unaltered. Neither could any evidence of its containing oxygen be derived from the action of potassium. (Phil. Trans. 1809.) But when exposed to the focus of a powerful lens in oxygen gas, it was observed that the gas became clouded during the process, and that there was a deposition of dew on the interior surface of the glass globe; a fact which indicates that plumbago, like charcoal, contains a very small quantity either of hydrogen or of water, which, in both, is probably rather an accidental than an essential ingredient.

Iron unites with various other metals. With potassium and sodium, it forms alloys more fusible and whiter than iron, and which effervesce when added to water. Stromeyer (81 Ann. de Ch.) has investigated the alloy of iron and silicium. It is formed by heating together iron, silica, and charcoal. The alloy is dissolved very slowly by acids, for it becomes covered with a coat of silica, which defends it from farther action, till it has been removed. Manganese forms a white and brittle alloy with iron. Iron also forms an alloy with tin; and iron plates, previously cleaned by a dilute acid, may be covered with tin by dipping them into that metal when melted.

## SECTION XVII.

*Tin.*

The properties of tin should be examined in the state of grain-tin or block-tin; what is commonly known by the name of tin being nothing more than iron plates with a thin covering of this metal. Several varieties of tin are met with in commerce; for the discrimination of which, and the means of judging of their purity, Vauquelin has given useful instructions in the 77th volume of the *Annales de Chimie*; and an interesting account of the ores of tin, and of the processes for extracting the metal in Cornwall, by Mr. Taylor, may be found in the 5th vol. of the *Geological Society's Transactions*. Cornish grain tin has been shown by Dr. Thomson to contain only a very minute proportion of foreign metals, never exceeding, and, for the most part, much less, than  $\frac{1}{500}$ th part, which is chiefly copper derived from the ore, sometimes a little iron, and a very minute portion of arsenic. (Thomson's *Ann.* x. 166.) Fischer, however, asserts that the very best tin contains occasionally a little iron, which enters with it into combination, and cannot easily be separated. To discover it, decompose a solution of the tin in question by ammonia, and separate the protoxide which falls down. Digest the precipitate in cold muriatic acid; nearly all the oxide dissolves, but if the portion which remains be removed, it will be found to contain but little oxide of tin, mixed with much oxide of iron. This portion dissolves in warm and concentrated muriatic acid, and the iron may then be discovered by tests. (Fischer in *Quart. Journ.* Mar. 1829.)

Tin has a silvery white colour, and by exposure to the air acquires a slight superficial tarnish, which does not appear to increase by time. Its specific gravity is about 7.9. It is extremely soft; scarcely, if at all, elastic; and, when a piece of it is bent backwards and forwards, it gives a peculiar crackling noise. It is very malleable, and may be beaten into leaves  $\frac{1}{1000}$ th of an inch thick. When heated a little below its fusing point, it is brittle, and its fragments exhibit a granular or fibrous structure.

Tin melts on the application of a moderate heat, equal to 442° Fahr. (Creighton); and if smartly agitated, while passing from a fluid to a solid state, it is finely granulated. It does not appear

to be volatile when strongly heated in close vessels, and it is by indirect methods that Dumas has calculated the density of its vapour at 4.053. When melted, it is converted by a long continuance of heat into a grey powder. This powder, which appears to be the first oxide of tin, when mixed with pure glass, forms a white enamel. The protoxide may be procured, also, by calcining, in a close vessel, the precipitate from fresh-made muriate of tin by carbonate of potassa. There is some difficulty in obtaining the protoxide pure, on account of its tendency to pass to the state of peroxide. Dr. Thomson recommends to add at once, to a solution of the protomuriate carefully prepared, as much pure potash as will saturate the acid. A black powder precipitates, which, when washed out of contact with air, and dried, continues in the state of protoxide. M. Cassola has given the following process as one which never fails. Upon filings of tin he pours nitric acid diluted with ten times its volume of water, and leaves the two substances in contact forty-eight hours. The tin acquires a brownish black colour, and is converted into protoxide. (Ann. of Phil. xiii. 40.) Tin is not oxidized at common temperatures, even by the concurrent presence of air and moisture.

The protoxide, when brought to a full red heat, takes fire; and, acquiring an increase of oxygen, passes to a pure white (yellowish, according to Thomson). This peroxide, when the heat is considerably raised, loses a part of its oxygen, and runs into fusion. The peroxide may be obtained at once by projecting tin into a crucible intensely heated, when the oxide rises in the form of flowers somewhat resembling those of zinc. It may also be procured, as Berzelius found, by distilling powdered tin with red oxide of mercury. It is insoluble in all the acids; but its hydrates, which are white, dissolve readily in muriatic, but not in nitric acid.

The oxides of tin have been investigated by Dr. Davy (Phil. Trans. 1812, 194), as well as by Gay Lussac, Berzelius, and Dr. Thomson, and their results very nearly agree. Gay Lussac states the composition of the protoxide to be,

Tin .....	88.10	.....	100.
Oxygen .....	11.90	.....	13.6

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100.

And that of the peroxide (Ann. de Chim. et de Phys. i. 43, and v. 151), in which he agrees with Klaproth,

Tin . . . . .	79	. . . . .	100.
Oxygen . . . . .	21	. . . . .	27.2
	<hr style="width: 10%; margin: 0 auto;"/>		
	100		

Dr. Thomson, by acting upon tin with nitric acid, found that 58 parts united with 16 of oxygen to become peroxide; and as Berzelius had proved that the protoxide contains just half the oxygen in the peroxide, the protoxide must be constituted of 58 tin, and 8 oxygen. Tin will, therefore, be represented by 58, the protoxide by 66, and the peroxide by 74.

Besides these two oxides, Berzelius suspects that an intermediate one is formed when tin is acted on by nitro-muriatic acid; and that it enters into the composition of deuto-muriate of tin. (87 Ann. de Chim. 50.) It has a yellow colour, and, from theory, should consist of 100 metal + 20.4 oxygen; but its existence is considered by Gay Lussac to be extremely questionable.

The oxides of tin have, in a certain degree, the properties of acids, so as to render it doubtful whether they should not be arranged in that class of compounds. But their affinities for bases are so feeble, that it seems advisable, on the whole, to retain them in the class of oxides.

The precipitates from solutions of tin by alkalis are *hydrates*, and have a white colour. They are soluble in an excess of fixed alkali; but the oxide is precipitated by the weakest acid, even the carbonic. The hydrates of tin are, also, decomposed by the action of boiling water. Dr. Thomson has described two hydrates, the one composed of two atoms of water, and one of oxide; the other, of one atom of peroxide, with four of water.

*Chloride of tin.*—Tin may be brought to combine with chlorine, by first forming six parts of it into an amalgam with one of mercury, triturating this with 30 parts of corrosive sublimate, and distilling the mixture from a glass retort into a well-cooled and capacious receiver, taking care to heat the retort very gradually. Or the same compound may be formed, according to Proust, by distilling a mixture of eight ounces of powdered tin and twenty-four ounces of corrosive sublimate. The result is a liquid formerly termed the *fuming liquor of Libavius*, which,

in a close vessel boils at 248° Fahr., and at ordinary temperatures emits dense white fumes, when exposed to the air. It gives no precipitate with muriate of gold or muriate of mercury; affords a yellow sediment with hydro-sulphuret of potassa; and dissolves a farther portion of the metal without effervescence. It acts on mercury, not in consequence of any excess of free chlorine, but because, abandoning one atom of chlorine, it is changed into proto-chloride of tin. It has the property of inflaming oil of turpentine, when suddenly poured into that liquid.

This compound, carefully examined by Adet, was proved to be a *per-chloride of tin*, perfectly free from water, and having a strong affinity for that fluid. Hence arises its fuming property; for the white vapours, which exhale when the bottle is unstopped, arise from the union of the salt with the moisture of the air. It may be formed at once, by heating tin in chlorine gas; and it consists, according to Dr. Davy, of 58 tin, and 72 chlorine, or,

					Atoms.	
Perchloride ..	Tin . . . .	44.61	. . . .	100	. . . .	1 = 58
	Chlorine	55.39	. . . .	122	. . . .	2 = 72
				100.		130

Dumas, from various considerations, is induced to regard it as constituted of 1 volume of the vapour of tin + 2 volumes of chlorine forming 1 volume of the perchloride. (Ann. de Chim. et de Phys. Dec. 1826.)

Another compound of tin and chlorine, called *proto-chloride of tin*, may be obtained by heating an amalgam of tin and mercury with calomel. It dissolves in water, and forms a solution, similar to the muriate of the protoxide, which rapidly absorbs oxygen from the air, and deposits peroxide of tin. It is composed of 58 tin and 36 chlorine, or

					Atoms.	
Proto-chloride ..	Tin . . . .	61.7	. . . .	100	. . . .	1 = 58
	Chlorine	38.3	. . . .	62	. . . .	1 = 36
				100.		94

*Chlorate of tin* is unknown.

*Iodide of tin*, formed either by the direct combination of tin with iodine, or by adding hydriodic acid to proto-muriate of tin, is an orange-coloured substance. The proportion of its elements has not been ascertained.



*Sulphate of tin.*—Tin dissolves in sulphuric acid, which takes up, when concentrated and heated, half its weight of that metal. It is dissolved also by this acid, diluted with about a fourth its weight of water, and heated. During both these processes, sulphurous acid is disengaged; and, in the latter, a pellicle of sulphur forms on the surface of the solution, which precipitates on cooling. When saturated, the solution deposits, after a while, needle-shaped crystals of sulphate of tin. If the sulphate be long boiled, a copious white precipitate subsides, which will not again dissolve. It is composed of the white oxide retaining only a small portion of acid, and constituting in fact a *sub-sulphate*.

*Nitrate of tin.*—When nitric acid highly concentrated is poured upon tin filings, very little effect is produced; but when a small quantity of water is added, a violent effervescence follows; and a bulky powder appears, which is the white oxide retaining a little acid. If more water be added, an acid liquor is obtained, holding very little tin in solution; and containing nitrate of ammonia, the alkaline base of which is formed by the simultaneous decomposition of the water and nitric acid, and the union of the hydrogen of the former with the nitrogen of the latter. Tin, however, is slowly dissolved, without effervescence, in nitric acid greatly diluted. The solution is yellow, and deposits oxide of tin by keeping.

*Muriate of tin.*—Muriatic acid, undiluted, is the proper solvent of tin. To one part of tin, in a tubulated retort, two parts of concentrated muriatic acid are to be added, and heat applied. The solution is complete, with the exception of a small quantity of black powder, which consists of protoxide of copper, (Thomson's Annals, x. 71;) and the acid takes up about one-fourth of its weight of tin.\* The solution has always an excess of acid; is perfectly limpid and colourless; and contains the metal at the minimum of oxidation. It has a tendency, however, to acquire a farther proportion of oxygen, and should therefore be carefully preserved from contact with the air. This property of absorbing oxygen is so remarkable, that it may even be applied to eudiometrical purposes. Proto-muriate of tin has, also, the

\* On the preparation of muriate of tin, see Berard, Annales de Chimie, xviii. 78; or Nicholson's Journal, xxvi.; and Chaudet, Ann. de Chim. et de Phys. iii. 376.

property of reducing iron to a minimum of oxidation, in those compounds, in which the metal is fully oxidized; for example, it reduces the red sulphate to the green. It is a test also of gold and platinum, as already noticed, and blackens the solution of corrosive sublimate. With hydro-sulphurets it gives a black precipitate.

When proto-muriate of tin is evaporated out of contact of air, a white salt may be obtained in large oblique four-sided prisms, transparent, of a silky lustre, and acid to the taste, and to colour tests. Making allowance for a little excess of acid and water, which are probably lodged mechanically between the plates of the crystals, it is composed according to Dr. Thomson (Edinb. Phil. Trans. 1827) of

Muriatic acid .....	1 atom	37
Protoxide of tin .....	1 atom	66
Water .....	1 atom	9
		112

Beside this, there is a *submuriate*, first described by Proust, and analyzed by Dr. Davy, consisting of

Muriatic acid .....	19.0	}	or probably	{	1 atom	37
Protoxide .....	70.4				2 atoms	132
Water .....	10.6				2 atoms	18
	100.				187	

Crystallized permuriate of tin consists of

Peroxide of tin ....	42.28	.... or 1 atom	= 74
Muriatic acid .....	42.28	.... or 2 atoms	= 74
Water .....	15.44	.... or 3 atoms	= 27
	100.	Weight of its atom	175

This is its constitution, as stated by Dr. Thomson (1st. Prin. i. 405). But in a paper printed in the Edinb. Phil. Trans. 1827, he reduces the muriatic acid to 1 atom, and the water to a proportion which would only amount to the fraction of an atom. Until this anomaly can be explained, I should therefore prefer his original analysis.

*Nitro-muriate of tin.*—The nitro-muriatic acid (formed by mixing two or three parts of muriatic acid and one of nitric) dissolves tin abundantly, with violent effervescence, and with so

much heat, that it is necessary to add the metal slowly by successive portions. The solution is apt to congeal into a tremulous gelatinous mass; and if water be added, it is partly decomposed, and some oxide separated. The solution, used by the scarlet dyers, is prepared with that dilute nitric acid called single aqua-fortis, to each pound of which are added from one to two ounces of the muriate of soda or of ammonia. This compound acid is capable of taking up about an eighth of its weight of tin.

*Acetate of tin.*—Acetic acid (distilled vinegar) by digestion with tin filings takes up a portion of the metal, and acquires an opalescent or milky appearance. The solution is decomposed by the action of the air, and deposits an insoluble oxide.

Tin dissolves in tartaric acid; and the solution is applied to the useful purpose of *wet-tinning*, the process for which is described in Aikin's Dictionary, ii. 427.

*Sulphurets of tin.*—Tin unites with sulphur, but requires, for its combination, so high a temperature, that at the moment of union there is too small a quantity of sulphur present, to saturate the tin, and a mechanical mixture results of tin and sulphuret of tin. The only method of obtaining the saturated sulphuret, is to melt the *aurum musivum*, which will presently be described, in close vessels. The *proto-sulphuret* is of a bluish colour and lamellated structure. It is composed of

Tin . . . . .	78.38	. . . .	or 1 atom	58
Sulphur . . . . .	21.62	. . . .	or 1 atom	16
	100.			74

The second sulphuret, or *bi-sulphuret* of tin (*aurum musivum*), is formed by heating sulphur with peroxide of tin, or by heating in a matrass a powdered amalgam of 12 parts of tin and 6 of mercury, mixed with 7 parts of flowers of sulphur and 6 of muriate of ammonia. A gentle heat is to be applied till the white fumes cease to appear, when the heat is to be raised to redness, and kept so for some time. On cooling, the *aurum musivum* may be obtained by breaking the matrass. It is of a beautiful gold colour, and flaky in its structure. Proust was of opinion that it is a sulphureted oxide; but Dr. Davy and Berzelius have shown that the tin is in a metallic state. According to the former, it consists of 59 tin + 32 sulphur, or,

Tin.....	64.5	} probably	{	1 atom ..	58
Sulphur .....	35.5			2 atoms	32
	100.				90

Berzelius, by redistilling bi-sulphuret of tin with sulphur, obtained a compound of a greyish colour and metallic lustre, which he found to be composed of tin and sulphur, in the proportion of 58 to 24. Hence it was a *sesqui-sulphuret of tin*.

Besides the true sulphurets of tin which have been described, Proust has described one, produced by precipitating proto-muriate of tin with sulphureted hydrogen, or by a hydrosulphuret. This Mr. Dalton believes to be a compound of 1 atom proto-sulphuret and 1 atom water, or, which is the same thing, of 1 atom protoxide + 1 atom sulphureted hydrogen. From solutions of the deutoxide, the same re-agents throw down a yellow compound, which Mr. Dalton found to consist of 1 atom of tin, 2 atoms of sulphur, and 1 of water. By a red heat, it loses one half its sulphur, and all its water. (New Syst. ii. 141)

Tin forms useful alloys with many of the metals. *Pewter* is one of these; and the best kind of it is entirely free from lead, being composed chiefly of tin with small proportions of antimony, copper, and bismuth.\* An amalgam, formed by gradually adding 3 parts of mercury to 12 of tin melted in an iron ladle, and stirring the mixture, is much used in the silvering of looking-glasses. A mixture of tin and lead, in about equal parts, composes the common *plumbers' solder*. Tin enters, also, into the composition of *bell metal and bronze*; and one of the most useful applications of it is to the tinning of iron plates, which is effected by dipping the plates into melted tin. The process, however, requires several preliminary steps, which are described in Bishop Watson's *Chemical Essays*, and in Mr. Parkes's *Essay in the Manchester Society's Memoirs*, vol. iii. N. S.

\* On the alloys of tin, a memoir of M. Dussausoy, may be consulted in the 5th vol. of *Ann. de Chim. et de Phys.*; and Mr. Chaudet's paper in the same and in the 7th volumes.

## SECTION XVIII.

*Cadmium.*

Cadmium was discovered, in the autumn of 1817, by Professor Stromeyer, of Göttingen, in an oxide of zinc, which had been prepared for medicinal use from an ore of zinc brought from Silesia. He ascertained its principal properties and combinations; and has since extracted it from various other ores of zinc. (Ann. of Phil. xiv. 269.) Dr. Clarke has shown that it exists in the ores of zinc from Derbyshire and Mendip, and in the zinc of commerce. (Ann. of Phil. xv. 272, and N. S. iii. 123.) Mr. Herapath of Bristol has also pointed out an abundant source of it in the sublimate, which, in the process for obtaining zinc by distillation, rises before the zinc, in what the workmen call the *brown blaze*. Of this sublimate, which is attached to the roof of the vault, it forms from 12 to 20 per cent. (Ann. of Phil. xiv. 435.)

The presence of cadmium, in an ore of zinc suspected to contain it, may be discriminated by directing the blue flame of a candle upon a small fragment placed on a slip of platinum foil. If any cadmium be present, its oxide will be reduced, volatilized, and carried along the slip of platinum, coating it with its peculiar reddish brown oxide. Dr. Wollaston, to detect cadmium, dissolves the ore of zinc in muriatic acid, gets rid by heat of the excess of acid, and adds distilled water. All the metals, that iron will precipitate, he removes by a rod of iron, and filters the liquor into a platinum capsule containing a piece of zinc. The cadmium, if any be present, will coat the surface of the capsule with a precipitate of a dull leaden hue, and will adhere so firmly that it may be washed, and thus freed from any remaining solution of zinc. Muriatic acid will dissolve the lead-coloured precipitate with effervescence, and either carbonated or caustic potassa will yield a white precipitate, which may be tested before the blow-pipe in the manner already described.

To separate cadmium from the ores of zinc, Stromeyer dissolves the ore in diluted sulphuric acid; and, through the solution, which ought to contain an excess of acid, sends a current of sulphureted hydrogen gas, which throws down sulphuret of cadmium. The precipitate is well washed, dissolved in concentrated muriatic acid, and the excess of acid

— expelled by evaporation. The residue is dissolved in water, and precipitated by carbonate of ammonia, an excess of which must be added, to redissolve any zinc or copper that may have been thrown down by the sulphureted hydrogen gas. Carbonate of cadmium alone remains, which, after being heated to drive off the carbonic acid, is reduced by mixing it with lamp-black, and exposing it to a moderate red heat in a glass or earthen retort.

Cadmium resembles tin very nearly in colour, lustre, and in the sound it emits when bent. It is somewhat harder than tin, and surpasses it in tenacity. It is very ductile, and may be reduced to fine wire, or thin plate; yet, when long beaten, it scales off in different places. Its specific gravity is 8.604 before hammering, and 8.694 afterwards; or, according to Mr. Children, 8.67 before, and 9.05 after, being hammered. (Quarterly Journal, vi. 226.) It melts at a heat below redness, and is volatilized by a heat not much greater than that required to vaporize mercury. Its vapour has no odour. It condenses in drops as readily as mercury, and these, on congealing, present distinct traces of crystallization.

Cadmium is as little altered by exposure to the air as tin. When heated in the open air, it burns as readily as the latter metal, and is converted into a brownish yellow oxide. This oxide, which is its only one, consists of 100 metal + 14.352 oxygen (Stromeyer), giving 56 for the equivalent number of the metal, and 64 for that of the oxide. This oxide is soluble in ammonia, but not in carbonate of ammonia, or in potassa or its carbonate, which even precipitate it from its solution in ammonia. By availing himself of this property, Mr. Children separated it from oxide of zinc, which is not thrown down by the fixed alkali, and thus verified its presence in compounds containing much zinc and little cadmium.

With the acids, oxide of cadmium unites and forms salts, which agree in the following characters. Fixed alkalis throw down a white hydrated oxide, as does ammonia, with this difference, that the latter, added in excess, redissolves the precipitate. Prussiate of potassa causes a white sediment, as does oxalate of ammonia. Sulphureted hydrogen, and the hydro-sulphurets, throw down cadmium of a yellow or orange colour, like orpiment. No change is produced by chromate of potassa, succinate or benzoate of ammonia, infusion of galls, or sulphate of soda.

*Chloride of cadmium* crystallizes in small rectangular prisms, perfectly transparent, which effloresce when heated, and are very soluble. At a high temperature it sublimes in small micaceous plates: 100 parts of the fused chloride consist of 38.61 chlorine + 61.39 metal. This gives 57 for the equivalent of cadmium, differing very little from the number deduced from the oxide.

*Iodide of cadmium* forms large and beautiful hexahedral tables, of a metallic or pearly lustre. At a high temperature the iodine escapes. It consists of 100 metal + 227.43 iodine.

*Nitrate of cadmium* crystallizes in prisms or needles, which are deliquescent. Its constituents are 100 acid + 117.58 oxide.

The *sulphate of cadmium* crystallizes in large rectangular prisms resembling sulphate of zinc, which are very soluble in water. They effloresce in the air, and at a gentle heat lose their water of crystallization, amounting to 34.26 on 100 of the dry salt. The neutral sulphate consists of 100 acid + 161.12 oxide.

The *carbonate* is pulverulent and insoluble in water, and readily decomposable by heat. It consists of 100 acid + 292.88 oxide.

The *phosphate* is pulverulent and insoluble. It is constituted of 100 acid + 225.49 oxide.

*Sulphuret.*—Cadmium unites with sulphur, as with oxygen, in only one proportion, which is that of 100 metal to 28.172 sulphur. The sulphuret has a yellow colour with a shade of orange. Concentrated muriatic acid acts readily upon it, and evolves sulphureted hydrogen gas. The sulphuret may be formed by heating sulphur either with the metal or the oxide, or by precipitating a solution of cadmium by sulphureted hydrogen.

*Phosphuret* of cadmium has a grey colour and a feeble metallic lustre.

Cadmium unites with other metals. Its alloy with copper is white, with a slight tinge of yellow. It unites also with cobalt, platinum, and mercury, and probably with other metals.

From a survey of its salts, it appears that their analysis does not lead to a perfect agreement as to the equivalent of its oxide, and consequently of that of the metal. None of the results, however, is very remote from affording 64 for the number

representing the oxide, from which deducting 8, we obtain 56 for the equivalent of cadmium.

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## SECTION XIX.

### *Arsenic.*

Arsenic, as it is found under that name in the shops, is not a metal, but a white oxide, or rather an acid, from which the metal may be obtained by the following process: Mix two parts of the white oxide with one part of black flux (prepared by detonating, in a crucible, one part of nitre with two of crystals of tartar), and put the mixture into a crucible. Invert over this another crucible; lute the two together, by a mixture of clay and sand; and apply a red heat to the lower one, keeping the upper one as cool as possible;—or the mixture may be introduced into a clean and dry Florence flask, which may then be set in a sand-bath, and gradually raised to a nearly red heat. The arsenic will be reduced, and will be found lining the inside of the upper crucible, or the upper part of the flask, in a state of metallic brilliancy, not unlike polished steel. Its specific gravity is 8.31. It is so extremely brittle that it may be reduced to powder by gentle pressure in a mortar.

Metallic arsenic is readily fusible, and is volatilized at 356°. In close vessels it may be collected unchanged; but when thrown on a red-hot iron, it burns with a blue flame and a white smoke; and a strong smell of garlic is perceived. This odour belongs to the metal only, and does not accompany the volatilization of its oxides. The density of the vapour of arsenic is calculated by Dumas at 5.1839.

### *Arsenic and Oxygen.*

Arsenic, by exposure to the air, is tarnished, and becomes converted into a bulky blackish powder. In three months, Berzelius found that 100 parts acquired an increase of 8.475; and he is disposed to consider the product as an oxidule, or sub-oxide; but it is probably nothing more than a mixture of arsenic and arsenious acid, into which, indeed, it is resolvable by heat. Only two combinations of arsenic and oxygen have hitherto been clearly ascertained; and both are possessed of acid properties.



The arsenious acid, or white oxide of arsenic (arsenic of the shops), has the following properties:

1. It is semi-transparent and brittle. Its specific gravity is 3.7. At a temperature of 380° Fahr. it is volatilized; or, if suddenly heated, it runs into a glass. It is highly poisonous, not only when taken into the stomach, but when applied to a wound, or when its vapour is inspired. Its vapour is quite inodorous.

2. Its taste had generally been represented as acrid and disagreeable; but Dr. Christison has shown that this is a mistake, and that, of several persons, the majority could perceive no taste, while a few thought it faintly sweetish. The solution also appeared, to most of those who tasted it, to be faintly sweetish. (Jameson's Edin. Journ. No. 5, p. 183.)

3. It is sparingly soluble in water. According to La Grange, it is soluble in one-twenty-fourth of cold water, or one-fifteenth of hot. Other statements have been given considerably differing from these; and Klaproth was, therefore, induced to examine its degree of solubility with great attention. A thousand grains of cold water, left in contact with the arsenious acid during 24 hours, and frequently agitated, dissolved only  $2\frac{1}{2}$  grains. But 1000 grains of boiling water took up  $77\frac{3}{4}$  grains; and, after being left three days to cool, and to deposit the crystals which separated, still retained in solution 30 grains. Bucholz has since published results, which agree, very nearly, with those of Klaproth. But the most elaborate experiments are those of Fischer of Breslau. According to these, arsenious acid is insoluble as such in water, and, when acted upon by water, one portion of the acid acquires oxygen from another, and, becoming arsenic acid, is rendered soluble. This is the reason why the undissolved portion loses its colour, and becomes of a dirty yellow. Of boiling water, according to Fischer, 12.3 parts dissolve 1 of arsenious acid; but, at the common temperature of the atmosphere,  $66\frac{1}{2}$  parts of water take up only 1 part. (Thomson's Annals, vii. 33.) The solution reddens vegetable blue colours. When slowly evaporated, the arsenious acid oxide crystallizes in regular tetrahedrons. It is also soluble in 70 or 80 times its weight of alcohol, and in oils.

4. The composition of the arsenious acid has been investigated by several chemists, with the following results. It consists,

	Arsenic.	Oxygen.	Arsenic.	Oxygen.
According to Proust, of ..	75.2	.. 24.8	.... 100	.. 32.979
————— Thenard, of ———	.. ———	.... 100	.. 34.694	
————— Berzelius,* of 75.81	..24.19	.... 100	.. 31.907	
————— Dalton .....		100	.. 33.3	

5. Arsenious acid combines with pure alkalis to saturation, and fulfils, therefore, one of the principal functions of an acid. Its compounds, called *arsenites*, may be formed by simply boiling the arsenious acid with the respective bases and a sufficient quantity of water. They have not been much examined. Those of potassa, soda, and ammonia, are soluble and incapable of crystallizing: those of lime, baryta, strontia, and magnesia, are difficultly soluble. Mr. Dalton finds that 28 parts of arsenious acid in solution are sufficient to throw down 24 parts of lime from lime-water, and to produce 52 parts of arsenite of lime, leaving the water free from both elements. (New Syst. ii. 66.) The metallic arsenites are best formed by mixing solutions of the alkaline arsenites with the metallic salts. Arsenite of ammonia, for instance, and nitrate of silver, afford a yellow precipitate of *arsenite of silver*, which is soluble in excess of ammonia; arsenite of potassa and sulphate of copper, an apple-green precipitate, called *Scheele's green*, which, when dried and levigated, forms a beautiful pigment. From salts of manganese, zinc, or tin, the same arsenite produces a white precipitate; and a dingy green one from salts of iron. Arsenite of lead, produced by mixing arsenite of ammonia and nitrate of lead, is composed, according to Berzelius, of 100 arsenious acid + 111.17 protoxide of lead.

### *Arsenic Acid.*

By repeated distillation with nitric acid, 100 parts of arsenious acid are changed into 115 or 116 of *arsenic acid*. The process, however, recommended by Bucholz is to mix 2 parts by weight of muriatic acid of the specific gravity 1.200 (?) 24 parts of nitric acid of the specific gravity 1.25, and 8 parts of white oxide of arsenic. The whole may be evaporated to dryness, and gently ignited in a crucible.

1. The arsenic acid has a sour, and at the same time a

\* Ann. of Phil. xv. 356.

metallic taste. It reddens vegetable blues; attracts humidity from the atmosphere, forming a liquid of sp. gr. 1.65 nearly; and effervesces strongly with solutions of alkaline carbonates. When evaporated, it assumes the consistence of jelly, and does not crystallize. It is a most active poison.

2. The composition of arsenic acid has been differently stated, as will appear from the following Table. It consists,

	Arsenic.	Oxygen.	Arsenic.	Oxygen.
According to Proust, of ..	65.4	.. 34.6	.... 100	.. 52.905
————— Thenard, of	64.	.. 36.	.... 100	.. 56.250
————— Berzelius, of	65.233	.. 34.717	.... 100	.. 53.179
————— Dalton	.....	.....	..... 100	.. 55.5

Dr. Thomson investigated the composition of arsenic acid by acting with nitric acid on a known weight of metallic arsenic. He found that 38 grains of the metal acquired 24 of oxygen, and became arsenic acid. He then ascertained how much oxygen was necessary to convert a given weight of arsenious into arsenic acid, and knowing the composition of the latter, it was easy to calculate that of the former. In this way he determined their constitution to be as follows:

	Arsenic.	Oxygen.	Atomic Wt.
Arsenious acid .....	1 atom +	2 atoms	.... 54
Arsenic acid .....	1 atom +	3 atoms	.... 62

So that the constitution of these acids resembles that of sulphurous and sulphuric. That arsenic admits of a degree of oxidation inferior to the lowest of these two, has not yet been proved by experiment, and is inferred chiefly from analogy. Admitting the composition of arsenious acid to be that which has been stated, the atomic weight of arsenic may be learned by deducting 16, the weight of 2 atoms of oxygen, from 54, when we obtain 38 for the equivalent number of arsenic. It is proper, however, to observe that Berzelius adopts a different view of the compounds of oxygen and arsenic, and contends that the oxygen of the arsenious is to that of the arsenic acid as 3 to 5. These proportions are admitted also by Mr. Dalton (New Syst. ii. 65), who is of opinion that the arsenic acid may be constituted of 2 atoms of a deutoxide of arsenic + 1 atom of protoxide.

3. Arsenic acid unites with bases, and constitutes a class of salts called *arsenates*, or *arseniates*. These salts resemble the

phosphates in this as in other respects, that though carefully neutralized when in solution, yet, when concentrated by evaporation, they crystallize with an excess of base.

*Binarsenate of potassa* was formed by Macquer by distilling in a retort equal weights of nitre and arsenious acid. It crystallizes in four-sided rectangular prisms, terminated by very short four-sided pyramids. It is permanent in the air, and has a saline and cooling taste. It is soluble in about five times its weight of cold water, but is insoluble in alcohol. It consists, according to Dr. Thomson, of

Arsenic acid, 2 atoms .....	124
Potassa, 1 atom .....	48
Water, 1 atom .....	9
	181

*Arsenate of soda* forms large crystals, having the same shape as those of phosphate of soda, which effloresce by exposure to a dry atmosphere. It has a cooling taste, resembling that of carbonate of soda, but less strong. It requires more than four times its weight of cold water for solution, and the liquid has alkaline properties. It undergoes the watery fusion. Its solution, when dropped into most earthy metallic salts, occasions precipitates, the peculiar appearances of which are exhibited by Dr. Thomson in a table published in the *Annals of Philosophy*, xv. 83. It consists of 1 atom arsenic acid, 1 atom of soda, and 8 atoms of water. There is also a binarsenate of soda, agreeing in the shape of its crystals with bi-phosphate of soda. These crystals consist of 2 atoms of acid, 1 of base, and 5 atoms of water.

*Arsenate of lime*.—Lime and arsenic acid were found by Mr. Dalton to unite in several proportions:

1st. 24 lime + 32.7 arsenic acid = insoluble arseniate.

2d. 24 lime + 49. arsenic acid = soluble arseniate.

3d. 24 lime + 98. arsenic acid = neutral arseniate.

*Arsenate of baryta* was prepared by Berzelius, by mixing nitrate of baryta with neutral arseniate of soda. It consists of

Arsenic acid .....	43.94	.....	100.
Baryta .....	56.06	.....	132.83

100.

*Sub-sesquiarseniate of lead*, made by double decomposition, was found to contain,

Arsenic acid . . . . .	25.25	....	100.
Protoxide of lead . . . .	74.75	....	296.04

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100.

And *arseniate of lead*, to consist of

Arsenic acid . . . . .	34.14	....	100.
Protoxide of lead . . . .	65.86	....	192.91

In the sub-salt, then, arsenic acid is united with one and a half time as much base as in the neutral arseniate of lead.

*Arsenic and chlorine*.—The compound of arsenic with chlorine, formed by distilling six parts of corrosive sublimate with one of arsenic, is a colourless fuming liquid. It was examined by Dr. Davy. (Phil. Trans. 1812, p. 188.) He determined its composition by synthesis, and states it to consist of

Chlorine . . . . .	60.48	....	100.
Arsenic . . . . .	39.52	....	65.3

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100.

This result, however, does not lead to an atomic weight for arsenic at all coinciding with that deduced from the oxides. Dumas thinks it probable that there exist two chlorides of arsenic. The first is formed by bringing dry chlorine gas into contact with metallic arsenic, gently heated. The gas is absorbed, and a liquid is produced; but in the parts of the apparatus where there is an excess of chlorine, a white crystallized matter appears, which is probably the perchloride. The first chloride may also be obtained by acting on arsenious acid with nascent muriatic acid. Into a tubulated retort, 30 or 40 parts of arsenious acid are put, along with 3 or 400 parts of strong sulphuric acid. When the temperature of the mixture has reached between 180° and 212° Fahr., small fragments of fused common salt are added. The proto-chloride falls in drops into the receiver, which should be artificially cooled. At first it is pure, but as the process continues, a hydrate of the proto-chloride is condensed, which, being lighter, floats above the true chloride. The watery ingredient of the latter may be separated by rectification from concentrated sulphuric acid.

The proto-chloride of arsenic is, when anhydrous, liquid, white, transparent, and a little fuming. By contact with water,

it is decomposed, and produces muriatic and arsenious acids. It boils at  $269^{\circ}$  Fahr. Its specific gravity exceeds that of water. The density of its vapour could not be ascertained, as it acts rapidly on mercury.

*Chlorate of arsenic* has not been examined, but chlorate of potassa and metallic arsenic afford a detonating mixture, which takes fire with amazing rapidity. The salt and metal, first separately powdered, may be mixed by the gentlest possible triture, or rather by stirring them together on paper with a knife-point. If two long trains be laid on a table, the one of gunpowder, and the other of this mixture, and they be placed in contact with each other at one end, so that they may be fired at once, the arsenical mixture detonates with the rapidity of lightning, while the other burns with comparative slowness.

*Iodine and arsenic* unite and form a deep red compound, which decomposes water, and affords arsenic and hydriodic acids. It is the subject of a memoir by M. Plisson. (Ann. de Ch. et Ph. Nov. 1828.)

*Arsenic and hydrogen*.—When tin is dissolved in liquid arsenic acid, an inflammable gas is disengaged, as was observed by Scheele, consisting of hydrogen gas, holding arsenic in solution. It may be obtained, also, by acting on an alloy of tin and arsenic with muriatic acid, or by adding powdered metallic arsenic to a mixture of diluted sulphuric acid and zinc filings, or by acting on water with a triple alloy of arsenic, potassium, and antimony. This alloy may be formed by heating strongly, for two hours, in a close crucible, two parts of antimony, two of cream of tartar, and one of white arsenic. When 2 or 3 drachms of this alloy are thrown quickly under a jar inverted in water, abundance of arsenureted hydrogen is disengaged. (Quart. Journ. xiii. 225.) The greatest caution should be used to avoid its deleterious effects, which were fatal to the late M. Gehlen. (95 Ann. de Ch. 110, and Ann. de Ch. et de Ph. iii. 135.)

This gas, to which the name of *arsenureted hydrogen* is best adapted, has the following properties:

(a) It is a permanently elastic and invisible fluid, of the specific gravity, compared with common air, of 0.5293; but its specific gravity is variable, in consequence of the admixture of different proportions of hydrogen gas. When pure, Dumas calculates its density at 2.695.

(b) It has a fetid smell, resembling that of garlic.

(c) It extinguishes burning bodies.

(d) It is sparingly taken up by water; and the solution has no effect on the blue colours of vegetables; but it is absorbed by solution of sulphate of copper, which may therefore be used to test its purity. In this way, Dumas found in some specimens of it from 69 to 70 per cent. hydrogen gas.

(e) It burns with a lambent white flame, and a disagreeable odour; and emits, during combustion, fumes of arsenious acid. Soap bubbles, blown with a mixture of this and oxygen gases, burn with a blue flame, a white smoke, and a strong alliaceous smell.

(f) When mingled with chlorine, heat is produced, a diminution ensues, and metallic arsenic is deposited.

(g) A stream of arsenureted hydrogen gas, issuing from a bladder fitted with a stop-cock, and set on fire in a large receiver filled with oxygen, burns with a blue flame of uncommon splendour.

(h) When 100 measures, in an experiment of Gay Lussac, were acted upon by heated tin, 140 measures of hydrogen were evolved; but, making due allowance for the mixture of free hydrogen, Dumas obtained an expansion, by the same process, of 100 volumes into 150. (An. de Ch. et de Ph. xxxiii. 356.)

For its perfect combustion, Dumas found that 1 volume of the pure gas requires 1.5 volume of oxygen, and that water and arsenious acids are the products. And as each volume of the gas contains 1.5 vol. of hydrogen, which requires 0.75 vol. of oxygen for combustion, the remaining 0.75 vol. of oxygen must have united with the arsenic. Hence 3 vols. of hydrogen, united with 1 vol. of the vapour of arsenic, are probably in this gas condensed into the space of 2 vols. In its combination with hydrogen, as well as with most other bodies, arsenic then presents a striking analogy to phosphorus.

A solid compound of hydrogen and arsenic may be formed by acting on water with an alloy of potassium and arsenic; and, of course, much less hydrogen gas is evolved than the same weight of uncombined potassium would liberate from water. It is described, by Gay Lussac, as separating in chesnut-brown coloured flocks. There appears, indeed, to be a strong affinity between hydrogen and arsenic; for Berzelius found that the recently-prepared metal, when distilled along with oxide of tin,

gave a drop or two of water. It must, therefore, have yielded hydrogen to the oxygen of the oxide.

*Sulphur and arsenic.*—The *sulphurets of arsenic* have been examined by Klaproth, Laugier (Ann. de Ch. et de Phys. v. 179), and Berzelius (Ann. of Phil. xv. 359). There are two sulphurets of this metal, both of which are found native, a red compound, called *Realgar*, and a bright yellow one, named *Orpiment*. They may also be formed artificially, the red by heating white arsenic with sulphur; the yellow by dissolving white arsenic in muriatic acid, and precipitating by hydro-sulphuret of ammonia. Laugier and Klaproth found

In realgar . . . . 100 arsenic united to 43.67 sulphur.

In orpiment .. 100 arsenic ——— 63.93 ditto.

It appears, therefore, that orpiment and realgar are both sulphurets of arsenic, containing sulphur in the proportions of 1 to  $1\frac{1}{2}$ , or of 2 to 3. Now these are the proportions in which oxygen, in the arsenious and arsenic acids, is united with arsenic. The quantity of sulphur, also, which, with 100 of arsenic, forms realgar, so nearly agrees with that of the oxygen, which with 100 of arsenic forms arsenious acid, that we may conclude them to correspond precisely; and the same may be observed of the quantities of sulphur and oxygen in orpiment and arsenic acid. Therefore,

In realgar . . . . . 100 arsenic are united with 42.11 sulphur.

In arsenious acid .. ————— 42.11 oxygen.

In orpiment . . . . . ————— 63.16 sulphur.

In arsenic acid . . . . ————— 63.16 oxygen.

If we consider realgar as the proto-sulphuret, orpiment will then be a *sesquisulphuret*, and the weight of the atom of arsenic, deduced from the proto-sulphuret, will still be 38, for 42.11 : 100 :: 16 : 38. Proportions very nearly agreeing with these have been derived by Mr. Dalton from his own experiments. In realgar he finds 100 arsenic + 45 sulphur; in orpiment, 100 arsenic + 64 sulphur. (New Syst. vol. ii.) Berzelius believes that there are not less than three sulphurets of arsenic; the two first of which, being the richest in sulphur, are respectively proportional to the arsenic and arsenious acids. Realgar, according to his view, is the lowest of these as to its proportion of sulphur, and orpiment is the one immediately above it. But the one which contains most sulphur has only been recently investigated. To these compounds he gives the name of *sul-*



*fide*, calling that which is analogous to arsenic acid, *sulfide arsenique*; that which is proportional to arsenious acid, *sulfide arsenieux*; and the third, *sulfide hypo-arsenieux*. Their compounds with bases are respectively *sulfo-arseniates*, *sulfo-arsenites*, and *sulfides hypo-arsenites*. The development of these views, and the description of the compounds to which they apply, form part of his memoir in the 32d volume of *Ann. de Ch. et de Phys.*

Orpiment is employed in calico-printing to deoxygenate indigo, which thus becomes capable of attaching itself to the cloth. M. Braconnot recommends realgar for dyeing wool, silk, or cotton, of a fine yellow colour. Having mixed one part of sulphur, two parts of white arsenic, and five of potash of commerce, melt them in a crucible at a heat near that of redness. The yellow mass thus obtained is to be dissolved in hot water, and filtered. It is then to be diluted, and sulphuric acid poured into it, of such strength as to produce a fleecy precipitate of a superb yellow colour. This dissolves with facility in ammonia, and gives a yellowish liquor, into which is to be poured an excess of ammonia for the purpose of discolouring it entirely. Goods plunged into this solution come out colourless, but they assume a fine yellow as the ammonia evaporates. The colour is durable, and resists acids, but not alkalis. (*Ann. de Ch. et de Ph.* xii. 98.)

*Alloys.*—Arsenic combines with most of the metals, which it generally renders brittle. With iron, zinc, and tin, it affords white brittle compounds. It unites with copper into a white alloy, as may be shown by confining a few grains of metallic arsenic, or of white arsenic mixed with black flux, between two copper plates, and heating them. The copper will acquire a white stain.

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## SECTION XX.

### *Molybdenum.*

The most common ore of molybdenum was long mistaken for plumbago, or carburet of iron, to which it bears externally a strong resemblance. It is, in fact, a combination of sulphur and molybdenum, the latter of which may be extracted by the

following process: To the ore of molybdenum, in a retort, six times its weight of nitric acid are to be added, and the mixture distilled to dryness. This process must be repeated four or five times; and at its close both the sulphur and molybdenum will be acidified. The sulphuric acid is expelled by heating the mass in a crucible; and any remaining portions are to be washed off with distilled water. The residue (*molybdic acid*) is a white heavy powder; which has an acid and metallic taste; has the specific gravity 3.4; is soluble in about 1000 parts of water; and forms salts with the alkalis and earths. The acid is reduced by making it into a paste with oil, and exposing it, bedded in charcoal in a crucible, to an intense heat. Or (as Hielm recommends), the ore of molybdenum may be repeatedly roasted in a moderate red heat, till the whole is reduced to a fine powder, which may be passed through a sieve. The powder is to be dissolved in ammonia, the solution filtered, and evaporated to dryness. The residuum, being moderately heated with a little nitric acid, gives a white powder, which is the pure oxide of molybdenum. This may be metallized by exposure to an intense heat with oil or powdered charcoal. Or lastly, as Berzelius recommends, over molybdic acid heated to redness in a porcelain tube, a current of hydrogen gas may be passed, as long as any water is produced. The residue is molybdenum in a metallic state.

Molybdenum has a yellowish white colour, but its fracture is a whitish grey. It has not, hitherto, been obtained in any form, but that of small brittle grains. It is almost infusible by any artificial heat. Its specific gravity is 8.611; according to Hielm it is 7.4.

It is readily oxidized when heated in contact with air, and is converted into a white oxide, which is volatilized in small brilliant needle-shaped crystals. This compound has acid properties.

The nitric and nitro-muriatic acids, and chlorine, are the only solvents that act on molybdenum. The muriatic, and other acids, act on its oxides, and afford blue solutions.

Until the late experiments of Berzelius, three oxides of molybdenum were generally admitted; the first, the *protoxide*, however, rather from analogy than from direct proof; the second, *molybdous acid*; and the third, *molybdic acid*. In these, the oxygen was deduced to be in the proportion of 48 molybdenum to 8, 16, and 24 oxygen respectively; and in-so far as molybdic acid

is concerned, this view corresponded very nearly with experiment, that acid consisting of

	Molybd.	Oxyg.
According to Bucholz . . . . .	100	50
———— Berzelius . . . . .	100	52.7

Now  $50 : 100 :: 24 : 48$ , the weight of molybdenum, on the supposition that the acid is a tritoxide. In that case the weight of the acid is  $48 + 24 = 72$ .

When one part of powdered molybdenum, and two parts of molybdic acid, are triturated in boiling water; then filtered; and the solution evaporated at a temperature not exceeding  $120^{\circ}$  Fahrenheit, we obtain a fine blue powder, which has been called *molybdous acid*. Dr. Thomson found that it is easily formed by heating together a mixture of molybdic and muriatic acids, and continuing the heat, till all the muriatic acid is driven off. This acid is more soluble in water than the molybdic, and its solution reddens vegetable blue colours. It is stated by Bucholz to consist of

Molybdenum . . . . .	74.5	. . . . .	100
Oxygen . . . . .	25.5	. . . . .	34
	—————		100.

The proportion of 34 to 100 is but little removed from that of 16 (2 atoms of oxygen) to 48, the atom of molybdenum. Berzelius, however, from recent experiments, is induced to consider molybdous acid, not as a distinct acid, since it does not combine with bases, but rather as a compound of two atoms of molybdic acid with one atom of deutoxide of molybdenum. This *deutoxide* he procures by digesting a mixture of molybdic acid, metallic molybdenum, and sulphuric or muriatic acid, till the colour of the liquid becomes a deep red. For metallic molybdenum, copper may be substituted. The red liquid gives, with ammonia, a rust-yellow precipitate, which is the *hydrated deutoxide*. When this is washed with water, the saline substances, which caused its precipitation, are first dissolved, and then the hydrate itself, giving a red liquid which reddens litmus. The hydrate dissolves in acids, and yields salts whose solutions are red, but which become black when evaporated to dryness. The deutoxide, freed from water, Berzelius finds to contain two atoms of oxygen, and molybdic acid three atoms of oxygen, to each atom of metal.

The protoxide of molybdenum is produced by macerating, with mercury, the solution of any salt with base of deutoxide, and adding from time to time a liquid amalgam of potassium. The colour of the liquid becomes deeper, and finally black. Before introducing the amalgam, muriatic acid must be added, in order to prevent a part of the deutoxide from being precipitated, before its entire reduction to protoxide. From the solution, ammonia throws down a black precipitate, which is a hydrate of protoxide. This is to be dried *in vacuo*.

The *anhydrous protoxide* is insoluble in acids. When heated in air, it takes fire, burns feebly, and produces a brown oxide. It is insoluble in acids, but the solutions of its hydrate afford black salts, which, when dissolved in water, have a green, black, brown, or fine purple colour. (Berzelius, Ann. of Phil. N.S. xi. 235.)

The molybdic acid, Berzelius observes, performs the part of a base towards the stronger acids. It unites, also, as is well known, with salifiable bases as an acid. Even when thus combined, it abandons part of its oxygen to bodies strongly attracting that principle; molybdate of potassa, for instance, is precipitated of a fine blue by proto-muriate of tin. The effects of a variety of reagents, upon solutions of that salt, are described in a Table published by Dr. Thomson (First Princ. ii. 58).

With chlorine, molybdenum unites in three proportions, forming compounds equivalent to its three oxides. The first is red and a little volatile. The second is black, very fusible, very volatile, and crystallizes in a black mass of a brilliant colour like iodine, which it resembles also in the colour of its gas. The third is colourless, and crystallizes in scales. (Berzelius.)

*Native molybdate of lead* from Carinthia, analyzed by Mr. Hatchett (Phil. Trans. 1796), contains 39.5 molybdic acid + 60.5 protoxide of lead, a proportion not very remote from that of 72 to 112, the equivalents of those two compounds, thereby confirming the view that has been taken of molybdic acid.

*Sulphuret.*—Molybdenum unites readily with *sulphur*. When one part of molybdic acid is heated with 5 parts of sulphur, we obtain a substance similar in composition to the native mineral, called molybdena. One hundred parts of the metal combine with 67 of sulphur, or 48 parts with 32; hence the compound is a bi-sulphuret. Berzelius has discovered also a

new sulphuret, proportional to molybdcic acid, and consisting of 1 atom of metal + 3 of sulphur. It is of a ruby colour, transparent, and crystallized. In the Ann. de Ch. et de Ph. xxxii. 393, a memoir of that writer may be consulted, in which he treats at great length of the compounds of sulphur with this metal.

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## SECTION XXI.

### *Chromium.*

This metal, discovered by Vauquelin in 1797, derives its name from *χρῶμα*, *colour*, all its compounds being beautifully coloured. It was at first found in an acidified state, combined with the oxide of lead, in the red-lead ore of Siberia; in the state of an oxide, in the green ore accompanying the red one; in the emerald, to which it communicates its green colour; and in some meteoric stones. A compound of oxide of chromium with oxide of iron has since been discovered in France, in America,\* and in Shetland,† and is a much more abundant product than the lead ore of Siberia, being found, in large masses, in Serpentine rocks. It is known in commerce by the name of *chromate of iron*; but this name is incorrectly applied. From a Table, exhibiting the results of nine different analyses of this ore, given by Dr. Thomson (Phil. Trans. 1827) it appears, in 100 parts to contain from 36 to 52 parts protoxide of chromium; from 24 to 35 parts of peroxide of iron, besides alumina, silica, &c., but no chromic acid.

To separate the chromic acid from red-lead ore, the ore, reduced to powder, is boiled with twice its weight of carbonate of potassa. An orange-yellow solution, composed of potassa and chromic acid, is thus obtained; and when, to this, a mineral acid is added, and the liquor is evaporated, we obtain, 1. the salt formed by the acid, which has been united with the potassa; 2. the chromic acid, in long ruby-coloured prisms. From this acid the chromium may be obtained by heating it intensely with charcoal, in the manner already often described. In the crucible a metallic mass is found, of a greyish white colour, formed of a number of needles crossing each other.

\* Thomson's Annals, v. 75. and N. S. iv. 76.

† By Dr. Hibbert. See his Description of the Shetland Islands, 4to.

The chromate of iron of commerce, however, from the greater plenty in which it is found, is a much cheaper source of chromic acid. After reducing this ore to fine powder, it is to be mixed with half its weight of nitrate of potassa, and heated strongly for an hour or two in a crucible. The oxide of chromium acquires a further dose of oxygen from the nitre, and is converted into chromic acid, which unites with the potassa. The mass is to be repeatedly digested with water, and the coloured liquids, which are slightly alkaline, saturated with nitric acid, and concentrated by evaporation, till no more crystals of nitre can be obtained from them. The yellow liquid, being now set aside for a week or two, deposits a copious crop of yellow crystals in small needles. These are to be separated, dissolved in water, and crystallized over again. They are then sufficiently pure chromate of potassa; a salt which, being now largely used in calico-printing, may, as well as the bi-chromate, be purchased at a moderate price. From the solution of these crystals, or indeed from the yellow liquid, proto-nitrate of mercury throws down an orange-red powder, which is chromate of mercury. When sufficiently heated, this compound is decomposed, and yields chromic acid, or oxide of chrome, from either of which metallic chromium may be obtained, by heating it violently with charcoal in a crucible.

### *Chromium.*

*The properties of chromium*, as described by Dr. Thomson from a specimen, with which he was furnished by Mr. Cooper of London, are the following. It is white with a shade of yellow, very brittle and easily reduced to a fine powder, which still retains the metallic lustre. It is not sensibly attracted by the magnet. Its specific gravity, generally stated at 5.9, was found by Dr. Thomson to be 5.093; but the specimen, which he tried, was by no means free from cavities.

In its metallic form, even though reduced to fine powder, it is scarcely acted upon by digestion in nitric or in nitro-muriatic acid. But when kept about 20 minutes in fusion with a sufficient quantity of hydrate of potassa and nitre, in the proportion of about five of the former to one of the latter, a yellow matter remains, which is soluble in water, and is in fact chromate of potassa. From this salt, brought by nitric acid to a neutral state, chromate of lead may be obtained, in such proportion, as, along

with other evidence, to show that the atomic weight of chromium is 32 on the hydrogen scale.

*Protoxide.*—By exposure to the combined action of heat and air, chromium is changed into an oxide. But the best way of obtaining the protoxide, is to reduce chromic acid, as it exists in its saline compounds, to a lower degree of oxidation. Many methods of doing this have been proposed. By digesting a solution of chromate of potassa with alcohol or tartaric acid, the chromic acid is speedily converted into green protoxide, and the same change is effected by boiling the dissolved chromate with muriatic acid and a little alcohol. The oxide thus obtained, after being washed and dried at the temperature of the air, is a greenish blue hydrate, containing  $\frac{1}{3}$ ths its weight of water. Dried on a sand bath, it still retains about one-half its weight of water, and acquires a beautiful green colour. In the first state, it is soluble in most acids, and is capable of forming neutral salts; in the second, acids, even by boiling upon it, are not neutralized. The green oxide, if heated nearly to low redness in an open vessel, generally glows, or becomes red-hot like burning tinder.

To determine the oxygen in this compound, Dr. Thomson carefully examined the amount of the loss which chromic acid (the equivalent of which was already known to be 52) sustains in becoming green oxide. By the employment of various methods, he was led to conclude that the atomic weight of the green oxide of chromium is 40. It is therefore strictly a protoxide, and is constituted of 1 atom of chromium + 1 atom of oxygen.

The salts, in which the protoxide of chromium acts as a base, have, according to Dr. Thomson, the following properties in common. The greater number have a deep green colour, though some of them are blue and a few are purple, and the intensity of their colour is such, that very dilute solutions of them are nearly opake. They have a strong and rather agreeable sweet taste. None of them can be crystallized.

Infusion of nut-galls gives, with the muriate, a green flocculent precipitate. Prussiate of potassa occasions no precipitate, but the liquid, when heated, becomes dark brown and opake. Sulphureted hydrogen has no effect on a solution free from chromic acid. Carbonate of ammonia and pure ammonia throw down the green oxide, as does caustic potassa; but the latter alkali, added in considerable excess, redissolves the oxide.

The individual salts with base of protoxide of chromium are fully described in Dr. Thomson's memoir.

*Brown Oxide.*—A brown compound of chromium and oxygen was first noticed by Vauquelin, and has since been supposed by some chemists to be a *deutoxide*, by others to be *chromous acid*. It may most conveniently be prepared, by passing a current of sulphurous acid gas through a solution of chromate or bi-chromate of potassa, and washing and drying the precipitate. It is of a flea-brown colour, not altered by exposure to air, destitute of taste, but capable of communicating an impregnation of chromic acid to a large quantity of water. In fact, it is nothing more, according to Dr. Thomson, (Phil. Trans. 1827) than a compound of 1 atom of chromic acid and 6 atoms of green oxide, and it is incapable of forming peculiar compounds. With these results, the experiments of Maus for the most part agree; but he finds that the relative proportions of green oxide and acid vary, according to the process by which the brown oxide has been prepared. (Ann. de Chim. et de Ph. xxxv. 216.)

The only definite proportions, then, in which chromium has been ascertained to unite with oxygen are the following:

	Chromium.	Oxy.	At. Wt.
1. Protoxide of chromium . . . .	1 atom	+ 1 atom	.. 40
2. Chromic acid . . . . .	1 atom	+ 2.5 atoms	52

The latter proportion of oxygen has hitherto been observed in no other instance, except in the hypo-sulphuric acid of Gay Lussac. To avoid the absurdity of fractions of atoms, we must consider chromic acid as constituted of 2 atoms of chromium and 5 atoms of oxygen.

*Chromic acid* is best obtained pure in the following manner: Mix chromate of potassa and nitrate of baryta in due proportions; an insoluble chromate of baryta will be formed; wash this with distilled water; then add a quantity of sulphuric acid, equivalent to the baryta in the nitrate, which has been employed; and, after digesting the mixture for a sufficient time, separate the liquid by filtration. From the solution, chromic acid is obtained by evaporation in fine ruby-coloured crystals. To free it entirely from sulphuric acid, an additional crystallization or two may be required. Dr. Thomson proposes another method of preparing this acid, by acting on the green oxide with nitric acid; and Maus obtains it by decomposing a hot and concentrated solution of bi-chromate of potassa with fluo-silicic acid;



filtering the liquid, and evaporating to dryness in a platinum capsule. He then dissolves the acid, thus dried, in the smallest possible quantity of water, to exclude a portion of fluosilicate of potash which has passed the filter, and decants the clear fluid; for in this state of concentration chromic acid cannot be filtered, as it attacks paper and is converted into oxide of chromium. (Quart. Journ. N. S. July 1828.)

Chromic acid has an intensely sour and metallic taste. It unites readily with alkaline, earthy and metallic oxide bases, and forms a distinct genus of salts. When exposed to heat in a closed glass tube, it yields oxygen gas; but Dr. Thomson found it difficult to expel, in this way, all its oxygen, and a small portion of the acid sublimed in an unaltered state. It is decomposed by protoxide of iron, and the acid in crystals decomposes ammoniacal gas, protoxide of chromium being produced in both cases.

*Chromate of potassa* forms crystals, the primary shape of which is a right rhombic prism. (Ann. of Phil. vi. 120.) Their colour is an intense lemon yellow, with a slight shade of orange. The colouring power of this salt is so great, that 1 grain in 40.000 grains of water forms a solution which is perceptibly yellow. Its taste is cooling, bitter, and very disagreeable, remaining long in the mouth. One hundred parts of water at 60° dissolve about 48 parts, but boiling water dissolves almost any quantity. It is insoluble in alcohol. Its solution in water decomposes most of the metallic salts; those of lead of a beautiful yellow colour, now much used as a pigment; those of mercury of a fine red; proto-salts of copper, brown; silver, dark red. According to Dr. Thomson, who has lately investigated it with much care, chromate of potassa is anhydrous, and is composed of

$$\begin{array}{r}
 1 \text{ atom of chromic acid} = 52 \\
 1 \text{ atom of potassa} \dots = 48 \\
 \hline
 100
 \end{array}$$

Tassaert, Jun. has endeavoured to show that this salt is in fact a *sub-chromate*, since it always affects colour tests like an alkali, and that in this respect chromium resembles arsenic and phosphorus, which also afford acids that form, with alkalis, only sub-salts or super-salts. (Ann. de Ch. et de Ph. xxii. 51.) It is not, however, the action of salts upon tests, but their atomic

constitution, that determines whether they are to be considered as neutral or otherwise.

*Bi-chromate of potassa.*—When to a solution of the chromate in water, such a quantity of sulphuric acid is added, as to give the liquor a sour taste, and it is set aside for 24 hours, small regular needles are deposited; or sometimes rectangular tables of considerable size, and of a beautiful orange-red colour. These crystals (figured by Mr. Levy, in Quart. Journ. xv. 287) are the *bi-chromate of potassa*. They are much less soluble in water than the chromate; for 100 parts at 60° Fahr. dissolve only about 10 parts. The solution has an intense orange colour, and reddens vegetable blues. The salt is composed of

2 atoms of chromic acid = 104	.....	68 421
1 atom of potassa . . . . .	= 48	..... 31.579
	<hr style="width: 10%; margin: 0 auto;"/>	<hr style="width: 10%; margin: 0 auto;"/>
	152	100.

The compounds of ammonia, potassa, soda, lime, and magnesia, with chromic acid, are soluble and crystallizable. The forms of the salts with base of soda and ammonia, are represented in the Ann. of Phil. vi. 286. Those of baryta and strontia are with difficulty soluble in water. The combination of chromic acid with various bases, and the properties of the resulting salts, have been fully described by Vauquelin in the 70th volume of Ann. de Chim.; by Dr. John in the 4th volume of the Annals of Philosophy; by Dr. Thomson in the 16th volume of the same work, and in the Phil. Trans. 1827; and by Grouvelle in the 17th volume of Annales de Chim. et de Physique. Some new double chromates, also, have been described by Mr. Stokes in the Phil. Mag., and Ann. of Phil. for December 1827.

*Chromate of chromium.*—With chromic acid, the protoxide of chromium, when in the state of perhydrate, readily unites, and forms a salt, the acid and base of which are both oxidized chromium. As protoxide of iron has the property of reducing chromic acid to protoxide of chromium, it is obvious that no protochromate of iron can exist; but with peroxide of iron that acid composes salts, in which the base is always more or less in excess.

*Uses of chromium.*—The principal use, to which chromium has been applied, is the preparation of the beautiful pigment, chromate of lead, known in commerce by the name of *chrome*

*yellow.* It is prepared by mixing the solutions of chromate of potassa and nitrate or acetate of lead. Nineteen parts of bi-chromate of potassa decompose 41.5 of dry nitrate of lead. The insoluble *chromate of lead* consists of 1 atom of chromic acid + 1 atom of protoxide of lead. (Thomson.) The application of chromium to dyeing and calico-printing was suggested, several years ago, by Lassaigne (Ann. de Ch. et de Ph. xiv. 299, xv. 76, and xvi. 400); and, in the latter art, very striking effects are now produced. By boiling together carbonate of lead with an excess of chromate of potassa, Dulong produced a red *subchromate of lead*. (Ann. de Chim. lxxxii. 292.) This Mr. Badams has shown to be constituted of an atom of chromic acid and 2 atoms of protoxide of lead, and he has proposed the use of it for giving a permanent scarlet colour to cotton. (Ann of Phil. N. S. ix. 303.)

#### *Chloro-chromic acid.*

This compound is described in Dr. Thomson's memoir on chromium, read before the Royal Society of London in March 1826. He there states that he had discovered it about a year and a half before his paper was written. In a letter from M. Dumas to M. Arago, dated May 6, 1826, and published in the Ann. de Chim. et de Phys. xxxi. 433, the same compound, under the name of *chloride of chromium*, is stated to have been formed by M. Unverdorben. The following account of it is derived from the memoir of Dr. Thomson, who seems to have pursued the farthest the investigation of its nature and properties:

Chloro-chromic acid is obtained with the greatest facility by the following process. Triturate together in a mortar 190 grains of bi-chromate of potassa, and 220 of common salt, till they are intimately mixed. Introduce the dry powder into a tubulated retort: insert the beak of it into a dry glass receiver, fitting it by means of a perforated cork, which should not be quite air-tight. Pour, into the retort, 500 grains of sulphuric acid of commerce, and by agitation make it into a paste with the salts. Then apply the flame of a lamp to the bottom of the retort. An effervescence takes place, and beautiful red fumes soon make their appearance. These are condensed in the beak of the retort, and gradually drop into the receiver under the form of a red-coloured liquid. This process lasts about ten or fifteen minutes, when the evolution of

the red fumes suddenly stops. The matter in the retort has now assumed a fine green colour, and the process must be suspended. The quantity of red liquid obtained is generally about 200 grains.

The red liquid has the following properties: Its colour is an intense but very beautiful crimson; so intense indeed, that, except in thin films, it is opaque. Its taste is sweetish, astringent, and acid. It has an odour of chlorine, fully as strong as chlorine itself. It however reddens vegetable blues.

Its specific gravity, as near as its extreme volatility would allow it to be determined, was 1.9134.

When dropped into water, it falls to the bottom; globules of chlorine issue from it copiously, and this continues till the red liquor dissolves in water, forming a yellow mass, which contains muriatic acid, chromic acid, and a little green oxide of chromium.

When dropped into alcohol, of sp. gr. 0.840, it sets it on fire. Poured on sulphur, a brisk action takes place which ends in the sulphur being inflamed. It does not, according to Dr. Thomson, act sensibly on phosphorus; but Dumas asserts that a drop of the fluid, and a piece of phosphorus not larger than a pin's head, act on each other with the evolution of heat and light, and detonate in larger quantities. It exhibits a brilliant combustion with ammoniacal gas, and muriates of ammonia and of chromium are formed.

The red liquid is not sensibly acted upon by charcoal, indigo, nitric or muriatic acids, iodine, oxygen, or chlorine.

By complicated methods of analysis, of which only the result need be stated here, Dr. Thomson found it to consist of

1 atom chromic acid . . . . .	52
1 atom chlorine . . . . .	36
	—
	Atomic weight 88

As water has the power of decomposing the red fluid, it is scarcely possible to combine it with bases.

#### *Fluo-chromic acid, or Fluoride of Chromium.*

By distilling fluor spar, chromate of lead, and sulphuric acid together in a leaden retort, M. Unverdorben obtained a gas which gave a dense yellow or red smoke, and on coming in contact with air, deposited small red crystals of chromic acid. The gas was collected by Berzelius in glass vessels coated with resin, which served to prevent its action on the glass, but only for a

short time. It was found to explode when mixed with ammoniacal gas. Water by absorbing the gas acquired an orange tint, and the liquid by evaporation afforded pure chromic acid, the fluoric being volatilized. When received into a platinum vessel, the inner surface of which was moistened with water, it deposited crystals of chromic acid, which had the singular property of exploding with a flash when heated to redness, and were resolved into protoxide of chromium and oxygen.

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## SECTION XXII.

### *Tungsten.*

In 1781, Scheele examined a mineral, known in Sweden by the name of *Tungsten* or *Heavy-spar*, and proved that it consists of a peculiar acid united with lime. (Essay xvii.) He detected, also, the presence of the same acid in another mineral called *Wolfram*, which has since been shown to contain also the peroxides of iron and manganese. (Berzelius. Ann. de Ch. et de Ph. iii. 261.) Various processes for extracting the tungstic acid from these native compounds have been described by Bucholz, in a memoir translated into the Ann. of Phil. vi. 198. It may be obtained from the tungstate of lime by digesting that mineral, very finely powdered, with three times its weight of nitric acid. This removes most of the lime, and leaves the tungstic acid in the form of a yellow powder, insoluble in water, but soluble by pure ammonia, with which it is next to be digested. The tungstate of ammonia is to be washed off and reserved; and the residue again boiled with a proportionately less quantity of nitric acid. These operations are to be alternated, till the whole of the mineral is decomposed. The ammoniacal solution, evaporated to dryness, and then ignited, yields tungstic acid.

There are several methods of obtaining tungstic acid from wolfram. Of these the most recent, and probably the best, is that described by Wöhler in the 29th volume of Ann. de Ch. et de Phys. A mixture of powdered wolfram and carbonate of potassa is fused; the tungstate of potassa is dissolved in water, and a sufficient quantity of muriate of ammonia then added. The liquor is evaporated to dryness, and the mass is fused in a Hessian crucible, till the muriate of ammonia is entirely decomposed and evaporated. By dissolving the fluid mass in water, a black powder separates, which is oxide of tungsten. This is

boiled with a weak solution of potassa, to remove a small quantity of acid and difficultly soluble tungstate of potassa, and then washed with abundance of distilled water. This oxide, when heated in an open crucible, burns vividly, and is changed into a yellow powder, which is tungstic acid.

Tungstic acid may be reduced to a metallic state, by heating it intensely with charcoal in the usual manner; but the process is a difficult one, and when it succeeds, the metal is obtained in only small granular particles.

Metallic tungsten has the following characters:

It has a greyish white colour, like that of iron, and a good deal of brilliancy. It is not magnetic. Its specific gravity, according to D'Elhuyarts, is 17.6; or, according to Messrs. Allen and Aikin, 17.22. Bucholz makes it the mean of these two numbers, *viz.*, 17.4. Tungsten is only, therefore, surpassed in density by gold and platinum. It is extremely hard and brittle. It requires, for fusion, a temperature of at least 170° Wedgwood.

Tungsten is oxidized by the action of heat and air. Its first oxide is flea brown. When heated, this burns like tinder, and is converted into the second, which is yellow, and is commonly termed *tungstic acid*.

The *tungstic acid* has no taste; its specific gravity is 6.12; it is difficultly fusible except by intense Galvanic action, which partially reduces it; it is insoluble in water; but remains suspended in it, and in this state has no action on vegetable colours. Exposed to heat in a platinum spoon, it assumes a deep green colour. Calcined with the contact of air, its yellow colour becomes deeper, and passes to a green, and, after some hours, to grey: but these changes of colour are not accompanied by any change of the relative proportions of oxygen and base. The deficiency of properties considered characteristic of acids, induced Vauquelin to withdraw it from the class of acids, and to arrange it among the oxides.

The tungstic acid is composed, as appears from the experiments of Bucholz, of 20 parts oxygen and 80 metal. Supposing the acid to consist of an atom of metal and three atoms of oxygen, this would give 96 for the equivalent of tungsten (for 20 : 80 :: 24 : 96) and 120 for that of tungstic acid.

By passing dry hydrogen gas over tungstic acid ignited in a glass tube, Berzelius obtained a chocolate-coloured powder, which

he found to be incapable of uniting either with acids or bases. When heated, it burned, and was converted into yellow tungstic acid, gaining such an addition to its weight, as to show that the oxygen of the acid is to that of the oxide in the proportion of 3 to 2.

Wöhler by converting metallic tungsten into tungstic acid, ascertained that 100 parts of the metal are acidified by 25 parts of oxygen, numbers which are precisely in the proportion of 96 to 24; and also that 100 parts of the oxide are converted into tungstic acid by eight parts of oxygen. Making, therefore, allowance for a small error, probably of manipulation, the compounds of tungsten and oxygen are as follows:

Oxide of Tungsten.	Tungstic Acid.
Tungsten .. 96 = 1 atom	Tungsten .. 96 = 1 atom
Oxygen . . . 16 = 2 atoms	Oxygen . . . 34 = 3 atoms
<hr style="width: 50px; margin: 0 auto;"/> Atomic weight 112	<hr style="width: 50px; margin: 0 auto;"/> Atomic weight 120

Dr. Thomson, from the analysis of some of the tungstates, deduces a much higher number, *viz.*, 150 for the atomic weight of tungstic acid, and  $150 - 24 = 126$  for that of tungsten. (First Princ. of Chem. ii. 70.) In this state of uncertainty, we can only reason from probabilities, which appear to me favourable on the whole to the view exhibited in the foregoing Table.

It is remarkable, Wöhler observes, that when tungstic acid, which is not free from a fixed alkali, is heated in contact with hydrogen gas, the product is not oxide of tungsten, but tungsten in a completely metallic state. The neutral tungstate of soda undergoes no change when ignited in hydrogen gas; but the acid tungstate of that base is converted into a compound of soda and oxide of tungsten, which, when a portion of the neutral salt is washed off by water, assumes a bright gold colour, and is capable of crystallizing in regular cubes. It consists, in 100 parts, of 86.2 oxide of tungsten + 13.8 soda. No analogous compound was obtained with base of potassa.

#### *Chlorides.*

*Tungsten and chlorine.*—The experiments of Wöhler lead him to believe that there are three *chlorides of tungsten*, but he has determined the composition of two only. The first is formed by heating the black oxide of tungsten in chlorine gas. The combination takes place with a disengagement of heat and

light, and a smoke arises, which is condensed into scales of a yellowish white, resembling native boracic acid. By the action of water, this substance is converted into muriatic and tungstic acids. It is therefore a chloride with the maximum proportion of chlorine.

The second chloride is formed, almost exclusively, when we heat metallic tungsten in chlorine gas; the metal burns; and the chloride appears either in fine needles of a deep red colour, or in a compact fused mass of the same colour, and having nearly the brilliant fracture of cinnabar. It easily melts, and enters into ebullition before being volatilized. Its composition seems to be analogous to that of the oxide, the chlorine in the former being equivalent to the oxygen in the latter.

Of the third chloride, little is known, and in one of the modes of its production (*vis.*, by the action of chlorine on sulphuret of tungsten) it is probable that chloride of sulphur must at the same time be formed, and be mixed with the resulting compound. (Ann. de Ch. et de Phys. xxix. 43.)

Berzelius examined the *sulphuret of tungsten*, with the view to determine the capacity of saturation of that metal. He heated together one part of powdered tungstic acid, and four of sulphuret of mercury. The mercury was expelled, and a blackish grey compound remained, not unlike sulphuret of copper. On analysis, it afforded

	Atoms.
Tungsten . . . . 74.891 . . . . 100. . . . 1 .. = 96	
Sulphur . . . . 25.109 . . . . 35.53 . . . . 2 .. = 32	
<hr style="width: 20%; margin: 0 auto;"/>	
100.	128

One hundred parts of the sulphuret, calcined so as to expel the sulphur and oxidize the metal, gave 93.5 of tungstic acid; and, as that quantity of acid must contain 74.891 metal, 100 acid should contain 80.09 oxygen, which agrees very nearly with the experiment of Bucholz. It may be remarked, that the sulphur in the sulphuret is double the oxygen in the oxide; and as the atomic weight of sulphur is twice that of oxygen, the sulphuret and the oxide are therefore equivalent compounds, both consisting of 1 atom of metal with 2 atoms of their remaining element.



## SECTION XXIII.

*Columbium.*

Columbium was discovered in 1801 by Mr. Hatchett, in a mineral belonging to the cabinet of the British Museum, supposed to be brought from Massachusetts, in North America. By alternate fusion with potassa, and digestion with muriatic acid, the mineral was decomposed; the acid combined with oxide of iron, and the alkali with a peculiar metallic acid, separable by diluted nitric acid, in the form of a copious white sediment. This acid was not reduced by Mr. Hatchett; but, from its properties, that excellent chemist entertained no doubt that it has a metallic base.

A metallic oxide, analogous in its properties to that of columbium, was discovered by Mr. Ekeberg, a Swedish chemist, in two different fossils, called Tantalite and Yttro-tantalite, both of which are found in Finland. To the metal obtained by reducing this oxide, he gave the name of *tantalum*. In the one it occurs combined with iron and manganese; in the other, with the earth yttria. (See Ann. de Chim. xliii. 281.) Beside these sources of columbium, Professor Hünefeld has discovered it, along with titanium, in the iron-slag of Königshütte, in Upper Silesia. (Phil. Mag. Feb. 1828.) The following are its characteristic properties, as described by Mr. Ekeberg: It is not soluble in any acid. Fixed alkalis, when fused with it in excess, act upon it, and dissolve a considerable quantity, which may afterwards be precipitated by acids, even by the carbonic. The oxide of this metal is white, and does not acquire any colour, by exposure to a high temperature with access of air; its specific gravity, after being made red-hot, is 6.500. It melts with phosphate of soda, and with borax, but does not impart to them any colour. When ignited with charcoal, it melts and agglutinates. It then presents a metallic lustre, and a shining fracture of a greyish black colour. Acids change it again into a white oxide.

Though the oxides of tin and of tungsten are equally soluble with that of tantalum in fixed alkalis, yet the former is easily reduced into a ductile metal; and the oxide of tungsten only dissolves in ammonia, is changed to a yellow colour by acids, and communicates colour to phosphate of soda and borax. The

oxide of titanium differs from that of tungsten, in being soluble by acids, and in tinging borax and phosphoric salts, when fused with them. (Thomson's Annals, iv. 467.)

Doubts had been entertained, whether any essential difference exists between columbium and tantalum; but their identity was at length fully established by the experiments of Dr. Wollaston. (Phil. Trans. 1809.) Having procured specimens of the tantalite and ytthro-tantalite, from which tantalum may be separated, he compared its properties with those of oxide of columbium, furnished by Mr. Hatchett, and also with those of a portion obtained by himself from the specimen in the British Museum. Both yield a white oxide, combined with iron and manganese, and as nearly as possible in the same proportion. The white oxide, though not absolutely insoluble in sulphuric, nitric, and muriatic acids, is (from whichever mineral it has been obtained) very nearly so. Its appropriate solvent is potassa, which does not require to be free from carbonic acid. By fusing 1 grain of the oxide with 8 of bi-carbonate of potassa, the whole of the oxide is dissolved, and may be precipitated by sulphuric, muriatic, or nitric acid, and it is not redissolved by an excess of acid. The oxides from both minerals agree, also, in being soluble, when fresh precipitated, by oxalic, tartaric, and citric acids. Infusion of galls, prussiate of potassa, and hydro-sulphuret of potassa, occasion no precipitation from the alkaline solution of either substance; and, when a sufficient quantity of acid has been added to neutralize the redundant alkali, infusion of galls only throws down a precipitate, which in both cases is of an orange colour. The identity of tantalum with the characteristic ingredient of columbium being thus established, it seems due, therefore, to its first discoverer, Mr. Hatchett, to distinguish it in future by the name which he applied to it.

To obtain metallic columbium, Berzelius introduced the acid, which had previously been strongly heated, into a cavity about one inch and a half deep, and of the diameter of a goose quill, artificially formed in a piece of charcoal. To this cavity a stopper of charcoal was fitted; and the whole, enclosed in a Hessian crucible, was exposed to a violent fire during an hour. On the average of four experiments, similarly conducted, he found that 100 grains of the acid gave 94.8 residue + 5.2 oxygen. On the supposition that the acid is composed of 1 atom of oxygen + 1 of metal, this would give 145.75 for the

atomic weight of columbium. But he has since ascertained that the metal, thus procured, still holds in combination from 7 to 8.4 (the mean of which is 7.7) per cent. of oxygen, and that only 3.9, on an average, of oxygen, are required for its full acidification. He considers, therefore, the product of the calcination of columbic acid in contact with charcoal as an *oxide*, the composition of which will presently be stated.

The specific gravity of a specimen of columbium, sent by Berzelius to this country, was found by Dr. Wollaston to be 5.61; but, as the mass was porous, its real specific gravity is probably much higher. Its colour was dark grey, and when scratched with a knife, or rubbed against a fine grindstone, it assumed the metallic lustre, and the appearance of iron. By trituration, it was reduced to a powder, which was destitute of metallic lustre, and completely insoluble, even by several days' digestion, in muriatic, nitric, or nitro-muriatic acid; but Berzelius has lately observed that fluoric acid dissolves columbium with a disengagement of hydrogen gas, and that a mixture of fluoric and nitric acids acts upon it with great energy. When heated below redness, the metal takes fire, and burns with a feeble flame; or if finely divided, it burns *vividly*, and is entirely acidified. It detonates, also, when mixed with nitre, and projected into a red-hot crucible. With other metals, it unites and forms alloys. (Ann. de Ch. et de Phys. iii. 140; Thomson's Annals, viii. 233.)

Another method, by which Berzelius has, more recently, decomposed columbic acid, is by acting with potassium on the fluo-columbate of potassa. The mixture, when heated, enters into ignition; fluat of potassa is formed; and may be separated by water from the revived metal. (Ann. de Ch. et de Ph. xxix. 303.) As several circumstances prevent the increase of weight, which the metal acquires by combustion, from being accurately determined, Berzelius investigated the composition of the acid by acting upon the sulphuret, artificially prepared. In this way, he ascertained the composition of columbic acid to be,

Columbium . . . . .	88.487	or	100.
Oxygen . . . . .	11.513	or	13.011

---

100.

Precipitated from muriatic acid by potassa, and dried at a gentle heat, columbic acid forms a hydrate consisting of

Columbic acid .....	88.83
Water .....	11.17
	100.

And the oxide, containing two-thirds of the oxygen in the acid, is composed of

Columbium .....	92.019	or 100.
Oxygen . . . . .	7.781	or 8.674
	100.	

If we admit, then, the atoms of oxygen, which, with an atom of columbium, constitute the oxide and the acid, to be in the proportion to each other of 2 to 3, the atomic weight of columbium will not be less than 184, for  $13.011 : 100 :: 24 (8 \times 3) : 184$ . But Dr. Thomson, by combining columbic acid with soda, and analyzing that salt, arrived at an equivalent number for columbium, very near that deducible from the first experiment of Berzelius. Columbic acid, he finds (First Princ. ii. 72), is represented by 19 on the oxygen scale = 152 (hydr. = 1) And deducting 1 atom oxygen ..... = 8

The atom of columbium is ..... 144

This number appears to be generally adopted by British chemists; but it is to be considered at present in the light merely of an approximation.

*Chloride.*—Columbium burns vividly in chlorine gas, and yields a yellow vapour, which condenses into a yellowish white powder. This, by contact with water, is converted with a hissing noise into columbic and muriatic acids.

*Sulphuret.*—Rose first prepared this substance by heating columbium at a low redness in the vapour of sulphur, or by transmitting the vapour of bi-sulphuret of carbon over columbic acid, in a porcelain tube heated to whiteness.

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## SECTION XXIV.

### *Antimony.*

Antimony, as it occurs in the shops, is a natural compound of that metal with sulphur. To obtain antimony in a metallic

state, the native sulphuret is to be mixed with two-thirds its weight of bi-tartrate of potassa (in the state of crude tartar) and one-third of nitrate of potassa deprived of water. The mixture must be projected, by spoonfuls, into a red-hot crucible; and the detonated mass poured into an iron mould greased with a little fat. The antimony, on account of its specific gravity, will be found at the bottom adhering to the scoriæ, from which it may be separated by a hammer. Or two parts of the sulphuret may be fused in a covered crucible with one of iron filings, and to these, when in fusion, half a part of nitre may be added. The sulphur quits the antimony, and combines with the iron.

In order to obtain antimony in a state of complete purity, the metal, resulting from this operation, must be dissolved in nitro-muriatic acid, and the solution poured into water. A white powder will precipitate, which must be dried, mixed with twice its weight of crude tartar, and fused in a covered crucible, when the pure metal will be produced.

Antimony in its metallic state (sometimes called *regulus of antimony*) is of a silvery white colour, very brittle, and of a plated or scaly texture. Its specific gravity, taken by Mr. Hatchett, was 6.712; by Dr. Thomson, 6.424. It is fusible by a heat of about 810° Fahrenheit; and crystallizes, on cooling, in the form of pyramids. In close vessels it may be volatilized, and collected unchanged; but not, Thenard asserts, if atmospheric air be carefully excluded, and no gaseous matter be generated during the process.

*Oxides of antimony.*—Antimony undergoes little change when exposed to the atmosphere at its ordinary temperature; but, when fused, with the access of air, it emits white fumes, consisting of an oxide of the metal. When a small fragment is placed on charcoal, and exposed to the flame of a blow-pipe supplied with oxygen gas, it burns with great brilliancy; and a dense yellow smoke of oxide arises from it. This oxide had formerly the name of *argentine flowers of antimony*. The vapour of water, brought into contact with ignited antimony, is decomposed with so much rapidity, as to produce a series of detonations.

Considerable differences exist among chemists, as to the composition of the oxides of antimony. According to Proust, (Journ. de Phys. lv.) they may all be reduced to two. The

first may be obtained by pouring muriate of antimony into water; washing the precipitate, first with a very weak solution of potassa, and afterwards with water; and then drying it. It has a dirty white colour, melts at a moderate red heat, and becomes opaque on cooling. The peroxide may be procured by collecting the flowers of antimony already described, or by acting on the metal with nitric acid, and expelling the redundant acid by heat; or by projecting powdered metallic antimony into red-hot nitre. This oxide is of a perfectly white colour, is less soluble in water than the former, less fusible, and may be volatilized at a lower temperature. The two oxides are composed, according to Proust, as follows:

The first of 100 antimony + 22.7 oxygen.

The second of 100 antimony + 30. oxygen.

Berzelius (86 Ann. de Chim. 225) has described four compounds of oxygen with antimony; but the first, obtained by the long exposure of the metal to a humid atmosphere, or by making that metal the positive conductor in a galvanic arrangement, which he has called *suboxide*, cannot be considered as a definite compound. The next, which is the true *protoxide*, may be obtained from muriate of antimony in the manner already described; or by boiling 50 parts of powdered metallic antimony with 200 of concentrated sulphuric acid to dryness; washing the residuum, first with a weak solution of potassa, and then with hot water, and drying; or by precipitating the compound called *emetic tartar* with pure ammonia, and edulcorating the precipitate with plenty of hot water. This oxide fuses at a red heat, and, on cooling, becomes an almost white mass resembling asbestos. It appears to be the only oxide of antimony which is capable of acting as a true base with acids, and is that which gives activity to the principal medicinal preparations of that metal.

The *second* or *white oxide* was formed by Berzelius by dissolving metallic antimony in nitric acid, and evaporating and igniting the product; or by dissolving the metal in nitromuriatic acid, decomposing by water, washing the precipitate, and calcining it in a platinum crucible. When calcined sufficiently, and not too much, its colour is perfect or snow white.

The *third* or *yellow oxide* was obtained by fusing a mixture of 1 part powdered metallic antimony and 6 of nitre, during an

hour, in a silver crucible, and washing the fused mass first with cold and then with boiling water. To the product, first evaporated to dryness, nitric acid was added, and the mixture digested several hours. A white precipitate was formed, which, whenedulcorated, dried, and gently heated in a platinum crucible, assumed a fine lemon-yellow colour. This is the *peroxide of antimony*. Dr. Thomson obtained it more simply by dissolving metallic antimony in nitric acid, evaporating to dryness, and exposing the product for some hours to a heat of 500° Fahr. A yellow powder remained, of which 7½ parts, exposed to heat, left 7 of white deutoxide; and 100 grains by distillation gave very nearly 19 cubic inches of oxygen gas. (Ann. of Phil. N. S. ii. 125.)

The composition of these oxides is thus stated by Berzelius :

	Metal.	Oxygen.	Metal.	Oxyg.
1. Protoxide . . . . .	84.32	.. 15.68	100	.. 18.6
2. Deutoxide . . . . .	80.13	.. 19.87	100	.. 24.8
3. Peroxide . . . . .	72.85	.. 27.15	100	.. 37.20
Ditto (corrected 1821) ..	76.34	.. 23.66	100	.. 31.

Dr. Thomson was led, by his experiments, to assign to these oxides the following proportions :

Protoxide . . . . .	100 metal	+ 18.2 oxygen.
Deutoxide . . . . .	100 do.	+ 27.3 do.
Peroxide . . . . .	100 do.	+ 36.4 do.

These numbers, it is evident, are more consistent with the general law of combination in multiple proportions than the later results of Berzelius; though they present, with respect to the deutoxide, the same anomaly as in the case of one or two other metals, *viz.*, that the multiple of the oxygen of the first oxide is 1½, and not an entire number. If Berzelius's analysis of the protoxide be correct, the equivalent number for antimony must be 43; but Dr. Thomson's determination would make it 44. Till its composition is decided, we may assume for

The equivalent number of antimony . . . .	44	
_____ of the protoxide ..	44 + 8 = 52	
_____ of the deutoxide ..	44 + 12 = 56	
_____ of the peroxide . . . .	44 + 16 = 60	

The peroxide is precipitated from its combinations in the form of a white hydrate, 100 grains of which, when exposed to

a red heat, give 5 grains of water, and 90.48 grains of deutoxide, the loss (4.52) consisting of oxygen. (Berzelius.)

The deutoxide and peroxide of antimony ought strictly to be arranged among acids, rather than among oxides; for each of them combines with salifiable bases, and affords a class of salts. The first has been called the *antimonious* acid, and its compounds *antimonites*; the second the *antimonic* acid, and the salts which it composes *antimoniates*. These names appear to me preferable to those which have been derived by Berzelius, from the Latin appellation *stibium*, viz., *stibious*, and *stibic acids*. For a detail of the properties of these saline combinations, I refer to the memoir already quoted, and to the 5th and 17th volumes of Ann. de Chim. et de Phys.

*Chloride of antimony*.—The combination of antimony with *chlorine* is best effected by distilling together  $2\frac{1}{2}$  parts of bi-chloride of mercury (corrosive sublimate) and 1 part of finely-powdered metallic antimony. The product may be rectified by a second distillation at a low temperature. It was formerly known by the name of *butter of antimony*. At common temperatures, it is a soft solid, which liquefies by heat, and crystallizes on cooling. It deliquates on exposure to the air, and, when poured into water, a precipitate falls, called *Algarotti's powder*, which is a *submuriate of the protoxide*. From this, the muriatic acid is removed by a weak solution of potassa, and the oxide, by drying, is obtained pure.

Chloride of antimony consists, according to Dr. Davy, of

Chlorine	.....	89.58	.....	100.
Antimony	.....	60.42	.....	150.13

But, as this compound is converted by water into protoxide and muriatic acid, it is evident that the chloride and protoxide must have a similar atomic constitution. M. Rose, therefore, submitted the solid chloride to a fresh analysis, the principal object of which was to determine its proportion of chlorine by the product of chloride of silver. By the method which he employed, the latter compound could not be obtained free from a little sulphuret of silver; but, without correction for this circumstance, chloride of antimony was inferred to consist of

Chlorine	.....	46.73	or 1 atom =	36
Antimony	.....	53.27	or 1 atom =	41.04



This would give 41 for the equivalent number of antimony, but we may consider that deduced from the protoxide (44) as entitled to greater confidence.

The substance obtained by acting on sulphuret of antimony with chlorine gas, M. Rose finds to be a mixture of the protochloride of antimony with chloride of sulphur.

Another chloride of antimony, according to M. Rose, is obtained by passing a current of dry chlorine gas over heated regulus of antimony. The antimony burns, emitting vivid sparks, at the same time that it yields a highly volatile liquid, which smokes in the air precisely like the *fuming liquor of Libavius*, with which it agrees also in forming a crystalline mass when a little water is added. When the new chloride is more largely diluted with water, it becomes hot, and deposits a powder, which is the *hydrated peroxide of antimony* or *antimonic acid*, constituted of 1 atom of metal + 2 atoms of oxygen. As the chloride then is changed into this oxide and muriatic acid, it must necessarily be constituted of 1 atom of antimony and 2 atoms of chlorine.

Dr. Thomson has also described a *di-chloride of antimony*, or compound of 1 atom of chlorine and 2 atoms of antimony. (First Princ. ii. 44.)

*Iodide of antimony* is of a dark red colour; and, when acted upon by water, yields hydriodic acid and oxide of antimony. A compound of iodine, antimony, and sulphur exists, also, containing an atom of each ingredient. (Quart. Journ. xviii. 397.)

*Salts of antimony.*—Antimony is soluble in most of the acids. When heated with *sulphuric acid*, the acid is decomposed; sulphurous acid is disengaged; and the antimony being converted into protoxide, a subsulphate is the product. *Nitric acid* dissolves this metal with great vehemence; but the most convenient solvent is the nitro-muriatic acid, which acts upon the metal both in a separate state, and as it exists in the black sulphuret. *Muriatic acid* acts on the latter compound, and evolves sulphureted hydrogen gas in abundance, and of great purity, and muriate of ammonia is also formed, and remains in solution along with the muriate of antimony. (Berzelius, Ann. de Chim. et de Phys. xvii.)

*Phosphate of antimony* has not been examined. The medicinal preparation, called James's powder, was found by Dr. Pearson to consist of 57 oxide of antimony, and 43 phosphate

of lime; and it has been imitated in *the pulvis antimonalis* of the London Pharmacopœia, which is formed by calcining the native sulphuret with hartshorn shavings. The preparation appears to be uncertain, and often even almost inert, and to vary as to the state of oxidation in the antimony, containing sometimes a large proportion of the peroxide. (See Mr. R. Phillips in Ann. of Phil. N. S. iv. 266, and vi. 187.)

*Tartarized antimony*, or *emetic tartar*, is a triple salt of protoxide of antimony, potassa, and tartaric acid. It is best prepared, according to Mr. R. Phillips (on the London Pharmacopœia, p. 80), by boiling 100 parts of metallic antimony to dryness with 200 of sulphuric acid. One hundred parts of the resulting subsulphate, boiled in an iron vessel with an equal weight of bi-tartrate of potassa, give at the first crystallization ninety parts of tartarized antimony; and a further quantity may be obtained by evaporating the solution. The primitive crystal of this salt is an octohedron with a rhombic base. (Ann. of Phil. N.S. vi. 40.) This salt ought to form, with a dilute solution of sulphuret of potassa, an orange-coloured precipitate.

In an elaborate memoir on tartarized antimony, read to the Royal Academy of Medicine at Paris, M. Henry discusses the merits of different methods of preparing it, and gives, on the whole, the preference to that of the Dublin Pharmacopœia, with a slight increase of bi-tartrate of potassa. He objects to the process of Mr. Phillips, that the quantity of subsulphate on which we operate is unknown; and the product, which he obtained by following that process, contained an excess of bi-tartrate of potassa. As the subject is interesting only to medical readers, I refer them, for a copious abstract of M. Henry's paper, to Dr. Duncan's Supplement to the Edinburgh New Dispensatory. (Edin. 1829.)

Dr. Thomson's analysis leads him to consider the constituents of emetic tartar to be

2 atoms tartaric acid, 66 × 2 . . . . .	=	132
3 atoms protoxide of antimony, 52 × 3	=	156
1 atom of potassa . . . . .		48
2 atoms of water . . . . .		18
		354

An atomic constitution differing considerably from this has been given by Dr. Gobel (Ann. of Phil. viii. 151), but the

analysis of Dr. Thomson is confirmed by one made some time ago by Mr. R. Phillips, though only lately published, except that the experiments of the latter give 3 instead of 2 atoms of water, making the atomic weight of tartarized antimony 363. (Same work, ix. 372.)

*Sulphuret of antimony.*—Antimony combines with *sulphur* by fusion, and forms an artificial sulphuret, exactly resembling the native compound. It may be procured, also, by passing sulphureted hydrogen gas through a solution of tartarized antimony. The proportions of its ingredients, as stated by Berzelius, with whom Rose agrees, are,

Antimony .....	72.86	....	100.	....	270
Sulphur .....	27.14	....	37.25	....	100
<hr style="width: 20%; margin: 0 auto;"/>					
100.					

Dr. Thomson's analysis makes it to consist of 44 metal + 16 sulphur, or of 100 metal + 36.36 sulphur.

When native sulphuret of antimony (frequently called *crude antimony*) is slowly roasted in a shallow vessel, it gradually loses its sulphur, the metal attracts oxygen, and is mostly converted into a grey oxide. This, being melted in a strong heat, acquires a reddish colour, and runs into a glassy substance, transparent at its edges, and termed *glass of antimony*. It consists of eight parts of protoxide and one of sulphuret, with ten per cent. of silica. The same quantity of oxide and two of sulphuret give an opaque compound, of a red colour, inclining to yellow, called *crocus metallorum*. With eight parts of oxide and four of sulphur, we obtain an opaque mass of a dark red colour, called *liver of antimony*. In all these compounds, the oxide is at its minimum of oxidation; for the peroxide is incapable of dissolving the sulphuret.

When fused with potassa, a triple compound is formed, composed of alkali, sulphur, and antimony. Or the combination may be effected, in the humid way, by boiling the powdered native sulphuret with pure potassa. The solution, on cooling, deposits an hydro-sulphureted oxide, in which the oxide prevails, called *Kermes mineral*. This compound, from Dr. Thomson's analysis, appears to be composed of 1 atom of protoxide + 1 atom of sulphureted hydrogen; but Rose considers it as having the same composition as the proto-sulphuret. The addition of a dilute acid to the cold solution, precipitates a

compound called *golden sulphur of antimony*, which may also be obtained by decomposing chloride of antimony with a sufficient quantity of hydro-sulphuret of potassa.

The *deuto-sulphuret of antimony* is obtained by passing sulphureted hydrogen through a solution of the deutoxide, which is best prepared by dissolving antimony in aqua regia, and evaporating the solution to dryness. The peroxide thus formed is, by ignition, converted into deutoxide; this is to be fused with caustic potassa, and the fused mass heated with muriatic acid and water, till a clear solution is obtained, which is to be decomposed by a current of sulphureted hydrogen gas. (Rose.)

The *persulphuret*, or *trito-sulphuret*, is identical with the golden sulphuret of antimony. It may be procured by well-known processes, and also by one contrived by M. Rose, which consists in passing sulphureted hydrogen through the perchloride of antimony diluted with water, to which tartaric acid has been added to prevent the water from causing precipitation. (Ann. de Ch. et de Ph. xxix. 241.) Another view, however, has been taken of this compound, which has been considered as consisting of 1 atom of protoxide of antimony + 1 atom of bi-sulphureted hydrogen.

*Alloys of antimony.*—Antimony enters into combination with most of the metals. It destroys the ductility of gold, even when it composes only  $\frac{1}{2000}$ th of the whole mass, or when merely its fumes come into contact with melted gold. The most important of its alloys is that which it forms with lead, called *type metal*. The composition of this alloy varies; the smallest types, Mr. Dalton finds, are cast from an alloy composed of nearly 1 atom of antimony to 1 of lead; middle-sized types of a compound of 1 atom of antimony and 2 of lead; and the largest size of 1 atom of antimony and 3 of lead. (New System, ii. 261.) Antimony may be alloyed with tin, but if its proportion in the alloy exceeds one-fourth, the tin loses its ductility. Tin, also, by combination with more than one-twentieth of its weight of antimony, acquires the insolubility of the latter metal in muriatic acid. (Ann. de Ch. et de Ph. iii. 380.) In analyzing compounds of tin and antimony, it is necessary first to make an alloy, in which the antimony shall not exceed the above proportion of one-twentieth part, for then concentrated muriatic acid, by digestion with this alloy, dissolves the tin, and leaves the antimony untouched.

## SECTION XXV.

*Uranium.*

URANIUM, in the state of an oxide, is occasionally found native and pretty pure in uran-ochre and uran-mica; but the scarcity of those minerals prevents their being employed for preparing the oxide in any considerable quantity. It is more commonly obtained from the mineral, in which it was originally discovered by Klaproth, called *pechblende*. In this, it exists along with iron, copper, lead, and sometimes with arsenic, cobalt, and zinc. The method recommended by Arfwedson enables us to free it from all those metals, and is as follows:

Finely-pulverized *pechblende* is dissolved, by means of a gentle heat, in a mixture of nitric and muriatic acids. When the decomposition of the mineral is completed, and most of the excess of acid expelled, a little muriatic acid is added, after which the liquid is to be diluted with a good deal of water. The sulphur, silica, and a portion of the gangue, remain undissolved. A current of sulphureted hydrogen must now be passed through the liquid, as long as any precipitate continues to fall. The liquid is now free from copper, lead, and arsenic, but contains iron, cobalt, and a little zinc. Let it be filtered, and digested with a little more nitric acid, to peroxidize the iron, when its colour will change to yellow. It must now be decomposed by carbonate of ammonia, added in excess, which will take up the oxide of uranium mixed with the oxides of cobalt and zinc, but leaves undissolved a great quantity of oxide of iron. The filtered solution is afterwards made to boil, and the boiling is continued as long as carbonate of ammonia is disengaged. A portion of the oxide of cobalt remains in the solution, which acquires a faint reddish colour; but another portion of it, and also the zinc, is precipitated along with the uranium. The precipitate is to be collected on a filtre, washed, and dried. It is then to be heated to redness, by which it loses its yellow colour, and becomes dark green. In this state it must be digested, some time, in dilute muriatic acid, which dissolves the oxides of cobalt and zinc, together with a small portion of peroxide of uranium. Pure protoxide of uranium remains undissolved, equal to about 65 parts from 100 of the mineral. (*Ann. of Phil. N. S. vii. 254.*)

Dr. Thomson dissolves the powdered mineral in nitric acid;

precipitates by sulphureted hydrogen; filters, and heats the solution to drive off the excess of that gas; and precipitates by caustic ammonia. After washing the precipitate, it is digested, while still moist, with a pretty strong solution of carbonate of ammonia. A fine lemon-yellow solution is obtained, and a red insoluble matter remains. The solution, being set aside during a few days, yields very fine rich yellow crystals, which are a triple salt of carbonate of ammonia, percarbonate of uranium, and water. From this salt, protoxide of uranium is obtained by exposing it to a red heat, in small grains, having a black colour and a good deal of lustre, but of a dark green colour when reduced to powder. (First Princ. of Chem. ii. 2.)

*Metallic Uranium.*—Arfwedson reduced the protoxide of uranium to a metallic state by exposing it, heated in a glass bulb, to a current of hydrogen gas. The reduction took place with such rapidity, that the matter became red-hot; and, at the end of the process, which lasted only a few minutes, the green protoxide was changed into a powder of a liver-brown colour.

This substance, which is probably metallic uranium, remains unaltered at the ordinary temperature of the atmosphere; but, when heated, it takes fire, swells, and is reconverted into green oxide. It is insoluble in muriatic and sulphuric acids, whether concentrated or diluted, but dissolves with facility in nitric acid, with an extrication of nitrous gas, and the solution has a lemon-yellow colour. One hundred parts of the protoxide lost, during this conversion, 3.53 or 3.54 of their weight, leaving a remainder amounting to 96.47 or 96.46. But  $96.46 : 3.54 :: 100 : 3.67$ , a loss corresponding with the increase of weight when the metal is heated to redness. On an average of several experiments, 100 parts of uranium, to become protoxide, combined with 3.688 parts of oxygen; and as this last number is to 100, so is 8 to 217, the atomic weight of uranium determined by these data. By the analysis of the triple salt, Dr. Thomson, however, arrived at 208 as the atomic weight of the metal; and he considers it as impossible, by Arfwedson's method, to come at the exact truth.

*Protoxide of uranium*, obtained from the percarbonate, is of a dirty green colour, but if again dissolved and thrown down by caustic ammonia, and then heated to redness, the protoxide is obtained in a black mass, the particles of which cohere strongly together. The concentrated acids dissolve it better than diluted

ones, and the solutions are green. Caustic ammonia precipitates the protoxide from these solutions in brown flocks inclining to purple, forming a hydrate; and when this is dried, the protoxide generally passes in great part to the state of peroxide. Carbonate of ammonia throws down from the proto-salts a light green precipitate of proto-carbonate of uranium, which is again dissolved by an excess of the precipitant. The hydrated protoxide dissolves very easily in acids, but if digested for an hour in water, the chemically combined water separates; the matter concretes into a heavy powder of small bulk, and is afterwards acted upon with great difficulty by acids.

*Peroxide of uranium* performs the double function of an acid and a base, and has so strong a tendency to enter into combination with other oxidized bodies, that it has not yet been obtained in an insulated state. If, for instance, we precipitate a solution of this oxide in nitric or muriatic acid by means of caustic ammonia, the precipitate is a combination of peroxide of uranium with ammonia and water, and is not decomposable by washing. It has probably a lemon-yellow colour, for this is the colour by which most of its salts are distinguished.

From the decomposition of uraniate of lead by exposing the anhydrous salt, ignited, to hydrogen gas, Arfwedson concluded that in the peroxide the oxygen is  $1\frac{1}{2}$  time as great as in the protoxide; and as in the protoxide 100 of uranium are combined with 3.688 oxygen, in the peroxide the proportion must be  $3.688 \times 1\frac{1}{2} = 5.532$ . Such, also, is the inference of Berzelius from the analysis of three of the salts of uranium. On the other hand, Dr. Thomson considers it to be determined, by his own careful analyses of several saline compounds of this metal, that the oxygen of the peroxide is double that of the protoxide, and that they are thus constituted:

	Uranium.	Oxygen.	At. Weight.
The protoxide of . . . .	1 atom	+ 1 atom	. . . . 216
or . . . .	100	+ 3.8461	
The peroxide of . . . .	1 atom	+ 2 atoms	. . 224
or . . . .	100	+ 7.6922	

It is evident then that we are not possessed of such clear evidence of the composition of the oxides of uranium, as of those of most other metals.

*Salts of Uranium.*—It is difficult to obtain the proto-salts of this metal pure, in consequence of the tendency of the protoxide to pass to the state of peroxide. The green solutions of the former

by the action of sulphuric and muriatic acids become speedily yellowish green and yellow, in consequence of the formation of peroxide, and the change is accelerated by adding a little nitric acid. The *pernitrate* is formed at once by dissolving the protoxide in nitric acid, and from this solution the *percarbonate* is thrown down by carbonate of ammonia. The pernitrate crystallizes easily in large flat four-sided rectangular prisms of a fine lemon-yellow colour. Its taste is acid and astringent, it reddens vegetable blues, and is exceedingly soluble both in water and alcohol, and is precipitated brown by prussiate of potassa. From Dr. Thomson's analysis, it appears to be a *sesqui-nitrate*, consisting of  $1\frac{1}{2}$  atom of acid, 1 atom of peroxide, and 17 atoms of water. The *persulphate* appears to have a similar constitution, with only 4 atoms of water; indeed the tendency of uranium to form sesqui-salts is very remarkable. It has also a great disposition to form double salts, such as the potassa-persulphate of uranium, the ammonia-persulphate, and the potassa-permuriate of the same metal. The peroxide possesses the properties of an acid, and probably forms definite compounds; this at least appeared to be true of the uraniate of potassa prepared by Dr. Thomson.

Among the *native compounds of uranium*, the green uranica appears, from the experiments of Mr. R. Phillips, to consist of phosphoric acid, peroxide of uranium, oxide of copper, and water; and the yellow, from the analysis of Berzelius, of similar ingredients, with the substitution of phosphate of lime for phosphate of copper. The first may be considered as a double sesqui-phosphate of uranium and copper, and the second of uranium and lime. Dr. John has discovered a native proto-sulphate of uranium in beautiful emerald green crystals, and a sub-persulphate, forming an intense sulphur-yellow coating over the surface of the minerals on which it is found. Hitherto uranium has not been applied to any useful purpose in medicine or the arts.

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## SECTION XXVI.

### *Cerium.*

Cerium was discovered in 1803, by Messrs. Berzelius and Hisinger of Stockholm, in a mineral from Bastnas, in Sweden, which had been supposed to be an ore of tungsten. From the



planet Ceres, discovered about the same period, it has been called Cerium; and the mineral that contains it is termed Cerite. (See Nicholson's Journal, xii. 105.) Cerium has since been found by Dr. Thomson to compose 40 per cent. of a mineral from Greenland, first distinguished as a peculiar species by Mr. Allan of Edinburgh, and thence called *Allanite*.

*Oxides*.—To obtain the oxide of this metal, the cerite, after being calcined and pulverized, is dissolved in nitro-muriatic acid. The solution is filtered, neutralized with pure potassa, and then precipitated by tartrate of potassa; or, as Laugier recommends, by oxalic acid. This precipitate, well washed, and afterwards calcined, is the oxide of cerium. The white oxide has been determined by Hisinger (Thomson's Annals, iv. 357) to consist of

Cerium	.....	85.088	.....	100.
Oxygen	.....	14.912	.....	17.41
		100.		

The peroxide, which is obtained by calcining the white oxide, is of a fallow red colour. It is composed of

Cerium	.....	79.29	.....	100.
Oxygen	.....	20.71	.....	26.115
		100.		

Hence it appears that the oxygen in the protoxide is to that in the peroxide very nearly as 2 to 3. If then we consider the former as constituted of 2 atoms of oxygen + 1 of metal, the equivalent for cerium will be 92; if of 1 atom only of oxygen + 1 atom of metal, the representative number of cerium will be 46; that of the protoxide 54; and that of the peroxide 62.

*Salts of Cerium*.—*Sulphuric acid*, diluted with four times its weight of water, dissolves the red oxide. The solution, on being evaporated, yields crystals, some of which are orange, and others have a lemon-yellow colour. The sulphate is soluble only by an excess of acid. Its taste is saccharine mixed with sour. Sulphuric acid readily unites also with the white oxide; the solution is nearly colourless, but has a slight rosy tinge. It has a sweet taste, unmixed with acidity, and yields white crystals.

From the analysis of the proto-sulphate of cerium, Dr. Thomson finds it to consist of

1 atom sulphuric acid .....	40
1 atom protoxide of cerium .....	58
3 atoms of water .....	27

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125

The number thus assigned to the protoxide of cerium is a little higher than that derived from Hisinger's analysis of the muriate; but admitting his proportion of the oxygen in the peroxide to that in the protoxide, their atomic weights will be as follows:

	Cerium.	Oxygen.	At. Weight.
Cerium .....			50
Protoxide ....	1 atom	+ 1 atom	58
Peroxide ....	1 atom	+ 1½ atom	62

*Nitric Acid* unites most easily with the white oxide. The solution is very sweet, and is not crystallizable. When decomposed by heat, it leaves a brick-coloured oxide.

*Muriatic Acid* dissolves the red oxide; and the solution crystallizes confusedly. The salt is deliquescent; soluble in an equal weight of water; and in three or four parts of alcohol. When this solution is concentrated, it burns with a yellow sparkling flame. The dry salt consists of 100 parts of muriatic acid united with 197.5 of oxide of cerium.

An infusion of galls produces, in muriate of cerium, a yellowish precipitate not very abundant. A few drops of ammonia throw down a very voluminous one of a brown colour, which becomes black and brilliant, by desiccation. By the action of heat it assumes a brick-red colour.

Oxide of cerium unites readily with *carbonic acid*. This union is best effected, by precipitating a solution of the oxide with carbonate of potassa. An effervescence ensues; and a white and light precipitate is formed, which assumes, on drying, a silvery appearance. It contains per cent. 57.9 parts of protoxide, 19.1 of water, and 23 of carbonic acid.

*Sulphuret*.—Sulphureted hydrogen does not unite with cerium; but cerium may be combined with sulphur, in two different ways. 1. By passing the vapour of carburet of sulphur over carbonate of cerium, a light porous compound is obtained, of the colour of minium, which is not altered either by air or water. 2. By fusing oxide of cerium with a great excess of hepar sulphuris, the latter of which is removed by washing. (Mosander, 33 Ann. de Ch. et de Ph. 109.)

*Properties of the metal.*—The attempts of Vauquelin to reduce the oxide of cerium produced only a small metallic globule, not larger than a pin's head. This globule was not acted upon by any of the simple acids; but it was dissolved, though slowly, by nitro-muriatic acid. The solution was reddish, and gave traces of iron; but it also gave evident marks of cerium, by the white precipitate which tartrate of potassa and oxalate of ammonia threw down. The metallic globule, also, was harder, whiter, much more brittle, and more scaly in its fracture, than pure cast-iron. When exposed by Mr. Children to his powerful Galvanic battery, oxide of cerium fused; and, when intensely heated, burned with a vivid white flame, and was partly volatilized. The fused oxide, on exposure for a few hours to the air, fell into a light brown powder, containing numerous particles of a silvery lustre. Hence cerium appears to be a volatile metal, unless it be volatilized in the state of an oxide, which remains to be decided by future experiments.

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## SECTION XXVII.

### *Cobalt.*

Cobalt may either be obtained from a substance sold under the name of Zaffre, by fusing the zaffre with three times its weight of black flux; or it may be purchased, at a moderate price, in a metallic form. It has been found by Stromeyer in a meteoric stone from the Cape of Good Hope, (Thomson's Annals, ix. 349,) and by others in stones of similar origin.

To obtain cobalt in a perfectly pure state, Tromsdorff recommends, that the zaffre should be, three times successively, detonated with one-fourth its weight of dry nitre, and one-eighth of powdered charcoal. After the last of these operations, the mass is to be mixed with an equal weight of black flux, and the cobalt reduced. The metal is then to be pulverized, and detonated with thrice its weight of dried nitre. This oxidizes the iron to its maximum; and acidifies the arsenic; which last unites with the potassa. Wash off the arseniate of potassa, and digest the residue in nitric acid. This will take up the oxide of cobalt, and leave the oxide of iron. Evaporate to dryness; redissolve in nitric acid; filter the solution; and decompose it

by a solution of potassa. The oxide of cobalt, now obtained, may be reduced by the black flux, as before directed. Dr. Thomson obtains the pure metal, more summarily, by the decomposition of the oxalate of cobalt. (Ann. of Phil. N.S. i. 250.)

Cobalt has a greyish white colour, inclining somewhat to pink. Its specific gravity is 8.538; it is brittle and easily reduced to powder; is not fusible with a less heat than  $130^{\circ}$  of Wedgwood; and, when slowly cooled, may be obtained crystallized in irregular prisms. It is magnetic, and was found by Wenzel to be convertible into a magnet, having all the properties of the magnetic needle. This quality, however, Mr. Chenevix imputes to its contamination with a small quantity of iron.

*Oxides of cobalt.*—By exposure to the atmosphere cobalt is tarnished, but not oxidized to any extent. In an intense heat it burns with a red flame; but, if pure, it is not easily oxidized by a moderate temperature. Its oxide, formed by long exposure to a strong heat with access of air, is of a deep blue, approaching to black. This, from the experiments of Thenard, appears to be the *protoxide*, which may be obtained, also, by precipitating the nitrate of cobalt with potassa. The precipitate, which at first is a bright blue hydrate, becomes, when dry, of so dark a blue as to appear black. It dissolves readily in muriatic acid, giving a solution which is green when concentrated, and red when diluted. Its solutions in sulphuric and nitric acids are always red.

When this oxide is exposed to the atmosphere, it gradually absorbs an additional quantity of oxygen; and becomes olive green. Treated with muriatic acid, it gives chlorine gas, and a red solution is obtained. This olive compound Sir H. Davy suspects to be a mixture of hydrate and oxide of cobalt, and not a peculiar oxide. When either of the two preceding oxides is heated in the open air, it passes to a flea-brown colour, which gradually becomes black. This is the metal oxidated to its maximum. The peroxide dissolves in muriatic acid, with a copious disengagement of chlorine. It is insoluble, however, in sulphuric and nitric acids, till it has parted with oxygen enough to reduce it to the minimum state. It is incapable, also, of being dissolved in pure alkalis, or of tinging vitrifiable mixtures blue.

The black or peroxide, heated for half an hour at the bottom of a crucible, loses a part of its oxygen, and is reduced to the state of protoxide. The protoxide is composed,

	Metal.	Oxygen.	Metal.	Oxygen.
According to Proust, of ..	83.5	.. 16.5	.... 100	.. 19.8
———— Rothoff	.... 79.56	.. 21.44	.... 100	.. 27.3
———— Thomson	.....			100 .. 28.5
———— Ditto (Atomic weight of cobalt 26)	100			.. 30.76

And peroxide of cobalt consists,

	Metal.	Oxygen.	Metal.	Oxygen.
According to Proust, of ....	75	.. 25	.... 100	.. 33.25
———— Rothoff	..... 71	.. 29	.... 100	.. 40.85
———— Thomson (At. wt. of cobalt 26)	100			.. 46.12

*Atomic weight.*—Rothoff ascertained that 100 parts of peroxide of cobalt, exposed to a strong heat, lose from 9.5 to 9.9. (Annals of Phil. iii. 356.) Taking the mean, 9.7, we have 100 of the peroxide composed of 9.7 oxygen + 90.3 protoxide, the oxygen in which, according to the same authority, is 19.3. Therefore  $9.7 + 19.3 = 29$ , is the oxygen in 100 of the peroxide; or 100 of the metal combine with 40.85 oxygen. Hence the peroxide contains  $1\frac{1}{2}$  times as much oxygen as the protoxide; for  $27.3 \times 1\frac{1}{2} = 40.95$  very nearly. If then the protoxide consist of 1 atom of metal + 1 atom of oxygen, the equivalent number for cobalt will be 30 (strictly 29.304); for the protoxide, 33; and for the peroxide, 42. From the analysis of the sulphate, Dr. Thomson has deduced that of the atom of protoxide to be 34; and on the supposition that the protoxide is composed of an atom of oxygen and an atom of cobalt, the atomic weight of cobalt will be 26. This number, however, is not consistent with the analysis of the oxides above stated, for in the peroxide it would increase the quantity of oxygen, united with 100 of metal, from 40.85 to 46.12. The true atomic weight of cobalt appears then to require further investigation.

*Chloride of cobalt.*—Cobalt takes fire when introduced, in a finely divided state, into chlorine gas; but the compound has not been examined. Mr. Brande, from the analysis of the chloride obtained by evaporating muriate of cobalt, infers that 100 of chlorine unite with 91.1 of cobalt; but this would give for the equivalent of that metal a higher number (32.54) than is deducible from the composition of the oxide.

*Salts of cobalt.*—*Sulphuric acid* does not attack cobalt unless when concentrated and heated; nor does it readily dissolve the oxide. They may, however, be brought to combine, and the result is a salt in oblique rhombic prisms, resembling sulphate of iron.

Dr. Thomson has described also a *bisulphate*, consisting of 2 atoms of acid, 1 atom of base, and 3 atoms of water.

*Nitro-muriate and nitrate of cobalt.*—The best solvents of cobalt are the nitro-muriatic and nitric acids; and the solutions have the property of forming sympathetic inks. One part of cobalt, or, still better, of zaffre, may be digested, in a sand-heat, for some hours, with four parts of nitric acid. To the solution, add one part of muriate of soda; and dilute with four parts of water. Characters written with this solution are illegible when cold; but when a gentle heat is applied, they assume a beautiful colour, which is invariably blue if the cobalt has been pure, or green if it contained iron or copper.\* This experiment is rendered more amusing, by drawing the trunk and branches of a tree in the ordinary manner, and tracing the leaves with a solution of cobalt. The tree appears leafless, till the paper is heated, when it suddenly becomes covered with beautiful foliage.

The crystals of *nitrate of cobalt*, are small and indistinct rhomboidal prisms of a deep red colour, composed, according to Dr. Thomson, of 1 atom of acid, 1 atom of protoxide, and 6 atoms of water. They are deliquescent in the air, and decomposable by heat, leaving a deep red powder. When thrown into a flask full of liquid potassa, a blue precipitate is formed, which, if the flask be immediately closed, passes to violet, and afterwards to red, by becoming the *hydrate* or *hydrated oxide* of cobalt. This compound is soluble in cold carbonate of potassa and tinges it red. The oxide is not soluble in this liquid. The hydrate loses from 20 to 21 *per cent.* of water by heat, and is reduced to protoxide. Solutions of cobalt are precipitated by carbonated alkalis, at first of a peach-flower colour, and afterwards of a lilac hue.

*Phosphate of cobalt* is formed by dissolving the carbonate in phosphoric acid, and adding alcohol, which throws down a bulky sediment, or by mixing muriate of cobalt and phosphate of soda. A lilac precipitate, in the last case, falls, which, if mixed with eight parts of fresh precipitated alumina, and dried, forms, according to Thenard, a blue pigment that may be substituted for *ultra marine*. (Quart. Journ. xv. 381.)

*Oxalic acid* throws down from solutions of cobalt a rose-

\* For some ingenious speculations on the cause of these phenomena, consult Mr. Hatchett's paper on the Carinthian molybdate of lead (Philosophical Transactions, 1796.)

coloured precipitate; *ferro-cyanate of potassa* one of a grass green colour; *solution of borax* a pink compound; and *hydro-sulphuret of ammonia* a black hydro-sulphuret of cobalt.

*Sulphuret.*—Cobalt may be brought to combine directly with sulphur and with phosphorus; but the compounds have no peculiarly interesting properties. The sulphuret is composed, according to Proust, who, however, does not place much reliance on his results, of

Cobalt	.....	71.5	.....	100.
Sulphur	.....	28.5	.....	39.8
				100.

If this analysis were correct, it would raise the atomic weight of cobalt to upwards of 33; for  $28.5 : 71.5 :: 16 : 33.71$ .

*Alloys.*—Cobalt may be alloyed with most of the metals, with the exception of bismuth and zinc; but its alloys have not yet been applied to any useful purpose.

Cobalt, when oxidized, is the basis of *zaffre*. This is generally prepared by roasting, from the ore, its volatile ingredients; and mixing, with the remainder, three parts of sand, or calcined flints. *Zaffre*, when fused, forms a blue glass; which, when ground and washed, is the substance termed smalts, used as a colouring substance for linen, and for imparting a blue colour to glass. These, and its application in the manufacture of porcelain, are the principal uses of cobalt in the arts.

## SECTION XXVIII.

### *Titanium.*

Titanium is obtained from a mineral discovered in Hungary, &c., called red schorl, rutile, or titanite; and its oxide, nearly pure, constitutes anatase or octohedrite. It is found, also, in a substance from Cornwall, termed menachanite; in octohedral iron ore from Corsica; in iserine; in sphene; in crichtonite; in black mica; in some feldspars and serpentines; and in the specular iron ore of Elba. Small pale yellow crystals from the diamond mines of Brazil, ascertained by Brogniart to agree in their form with anatase, were found by Vauquelin to be perfectly pure oxide of titanium. (Quart. Journ. xxii. 409.) It was in menechanite that it was originally discovered by Mr. Gregor of Cornwall; and its characters have since been more

fully investigated by Klaproth, Vauquelin and Hecht, Lovitz, Lampadius, and Rose. To separate it from titanite, the mineral is to be reduced to powder, and fused with twice its weight of potassa. When the fused mass, after cooling, is dissolved in water, a white oxide of titanium remains. To free it from iron, Laugier dissolved this oxide in muriatic acid, and added oxalic acid, which separates a white flocculent precipitate of oxalate of titanium. (89 Ann. de Chim. 306.) The oxalic acid in this may be destroyed by calcination. Menachanite is to be first fused with potassa in a similar manner; and to the alkaline solution, muriatic acid is to be added. This dissolves the oxide of iron, and precipitates the white oxide of titanium, still, however, contaminated by some iron.

Rose has more lately advised to add tartaric acid in excess to the mixed solutions of oxide of iron and titanitic acid in muriatic acid. After this, ammonia, added in great excess, causes no precipitation, but from the solution so supersaturated, hydrosulphuret of ammonia throws down all the iron, without affecting the titanitic acid. This acid may be obtained by evaporating the filtered liquid, and calcining the dry mass with free contact of air. (Ann. de Ch. et de Ph. xxix. 131.) To separate titanitic acid from titanized iron, which may be had in greater plenty than rutile, he exposes that mineral finely powdered, and heated in a porcelain tube, to sulphureted hydrogen gas. The iron is deoxidized and converted into a sulphuret, but the titanitic acid remains unaltered. After cooling, the mass is digested in concentrated muriatic acid, much sulphureted hydrogen is disengaged, and sulphur is deposited, which, mingling with the titanitic acid, gives it a grey colour. The acid is washed, dried, and ignited, to expel the sulphur. This operation it may be necessary to repeat, in order to remove all the iron. (Ann. de Ch. et de Ph. xxxviii. 131.)

Oxide of titanium fuses, but is not reduced by a powerful Galvanic battery. It is indistinctly metallized, by exposure to an intense heat, moistened with oil, and surrounded by powdered charcoal. A blackish blistered substance is obtained, some points of which have a reddish colour. Lampadius states its colour to be that of copper, but deeper; and its lustre to be considerable. The evidence of the reduction of titanium to a metallic state was not, however, satisfactory, till the attention of Dr. Wollaston was drawn, in 1822, to certain very small cubes, having the



lustre of burnished copper, that are occasionally found in the slag of the great iron works at Merthyr-Tydvil in Wales, at Low Moor in Yorkshire, and in various other places. (See 31 Ann. de Ch. et de Ph. 331, and Phil. Mag. Feb. 1828, p. 121.) These cubes are distinguished from iron pyrites by their colour, as well as by their extreme hardness, which is such that they even scratch rock crystal. They conduct electricity and are slightly magnetic. Their sp. gr. is 5.3. They are not acted upon by muriatic, nitric, nitromuriatic, or boiling sulphuric acid. Before the blow-pipe they are completely infusible. A long continued heat oxidizes them, and they become purple or red at the surface. Nitrate of potassa, aided by a strong heat, oxidizes them rapidly. The combined action of equal quantities of borax, and dried sub-carbonate of soda, with the assistance of a strong heat, yields a fused mass, which becomes opaque by cooling. This may either be previously freed from the salts by boiling water, and then dissolved in muriatic acid, or the whole mass may be dissolved together. In either case, alkalis throw down a white oxide, which is not soluble by excess of alkali, either pure or carbonated. By evaporating the muriatic solution of the oxide to dryness, at the heat of boiling water, it is freed of any redundant acid, and the muriate, which remains, is perfectly soluble in water, and in a state most favourable for exhibiting the characteristic properties of the metal. There can be no doubt, then, that these cubes are metallic titanium, free from contamination, except with a portion of iron, so minute as to be scarcely discoverable by tests, but sufficient to impart a very slight magnetic property.

*Oxides.*—Titanium appears capable of uniting with oxygen in two proportions. The *protoxide* is blue, and occurs native in crystals called *anatase*. We know, however, very little of the properties of this oxide. The *peroxide* is perfectly white, and, possessing some of the properties of a weak acid, it is named by Rose, (Ann. of Phil. N. S. vi. 369, and 29 Ann. de Ch. et de Ph. 130) *titanic acid*. Like columbic acid and silica, which last Rose considers as an acid, its affinities are exceedingly weak. When heated to redness, it becomes yellow, but regains its whiteness on cooling; it is found, however, to have become insoluble in acids. When fresh precipitated titanitic acid is digested with water, the liquid passes milky through several folds of paper. Hence it cannot be collected on a filter, unless we add to the

liquid an acid, an alkali, or a neutral salt. When fused with potassa, and dissolved in muriatic acid, it gelatinates.

Titanic acid or peroxide of titanium has been considered as a base capable of forming neutral salts with acids, but Rose is disposed to deny to it this property, and supposes that what has heretofore been regarded as pure titanic acid is, in fact, a compound of that acid with an alkali. No compounds, he conceives, exist, in which titanium can be considered as a base.

*Chloride of titanium* was formed by Mr. George, by passing dry chlorine over the pulverized cubes from the iron slag. A fluid condensed in the cool part of the tube, which was transparent, colourless, emitted dense white fumes, and boiled violently at a temperature little exceeding  $212^{\circ}$  Fahr. ( $275^{\circ}$  Fahr. Dumas.) On adding a drop of water to a few drops of this liquid, an almost explosive disengagement of chlorine ensued; and when the water was not in excess, a solid salt was formed, the solution of which had all the properties of muriate of titanium. There appears, from these experiments, to be two chlorides, the one constituted of about 64 titanium with 36 chlorine, the other with 72. (Ann. of Phil. N. S. ix. 18.)

Dumas also, led by the analogy between tin and titanium, as traced by Mitscherlich in the isomorphism of their native oxides, effected the combination of titanium with chlorine by passing the latter over pure oxide of titanium mixed with 1-4th of charcoal and ignited in a porcelain tube. A white, excessively fuming, and very volatile chloride was obtained, of specific gravity exceeding that of water. The density of its vapour he calculates at 7.047, and he believes it to be constituted of 1 vol. of vapour of titanium + 2 vols. of chlorine condensed into 1 vol. (33 Ann. de Ch. et de Ph. 386.)

Titanium is precipitated of a red, inclining to orange, by ferrocyanate of potassa; of a similar colour by infusion of galls, but inclining to purple; and of a dirty dark green by hydrosulphurets. A rod of tin, immersed in the solution, imparts to the liquid surrounding it a fine red colour, and a rod of zinc a deep blue colour.

*Sulphuret of titanium* was formed by Rose, by passing sulphuret of carbon over titanic acid strongly heated in a porcelain tube. It is of a deep green colour, and, when rubbed with a hard substance, assumes a very strong metallic lustre like that of brass. It becomes very hot when nitric acid is poured upon

it; nitrous gas is disengaged, and titanitic acid is deposited in the state of a fine powder. The analysis of the bi-sulphuret by combustion gave

Titanium .....	49.17
Sulphur .....	50.83
	100.

And that of the titanitic acid,

Titanium .....	66.05
Oxygen .....	33.95
	100.

From a review of the experiments of Rose, and his own investigations, Dr. Thomson believes 48 to be the true atomic weight of titanitic acid, 40 to be that of the protoxide, and 32 that of titanium. (First Princ. ii. 80.) But Dumas is disposed to consider titanitic acid as 1 atom of titanium + 1 atom of oxygen. This point can only be decided by further experiments, for which the chloride appears well adapted.

Dr. Wollaston attempted to form alloys of titanium with tin, lead, silver, and copper, but did not succeed with respect to any one of them.

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## SECTION XXIX.

### *Bismuth.*

Bismuth has a reddish white colour, and is composed of broad brilliant plates adhering to each other. Its specific gravity is 9.822, but is increased by hammering. It breaks, however, under the hammer, and hence cannot be considered as malleable; nor can it be drawn out into wire. The bismuth of commerce is not quite pure. To purify it, Dr. Thomson dissolved it in nitric acid, decomposed the nitrate by water, edulcorated the oxide, and reduced it to a metallic state by heating it in a covered crucible with black flux.

Bismuth is one of the most fusible metals, melting at 476° Fahr.; and it forms, more readily than most other metals, distinct crystals by slow cooling. M. Chaudet has shown that, though covered with charcoal, it may be completely volatilized, if kept for a sufficient time at a temperature of about 30° Wedgwood

*Oxide.*—When kept melted at a moderate heat, it becomes covered with an oxide of a greenish grey or brown colour; in a more violent heat bismuth is volatile, and may be sublimed in close vessels; but, with the access of air, it emits a blue flame, and its oxide exhales in the form of a yellowish smoke, condensable by cold bodies. This oxide is very fusible; and is convertible, by heat, into a yellow transparent glass. It is the only oxide of bismuth with which we are acquainted; and consists, according to the experiments of Lagerhjelm, (4 Ann. Phil. 357) of

Bismuth	..... 89.863	..... 100.	..... 71
Oxygen	..... 10.137	..... 11.28	..... 8
	100.		79

Dr. Thomson dissolved 9 grains of purified bismuth in nitric acid, evaporated the solution, and heated the dry mass till it was reduced to the state of an oxide. It became 10 grains; consequently the metal had combined with one ninth its weight of oxygen; and  $1 : 9 :: 8 : 72$ . We may adopt then 72 as the atomic weight of bismuth and 8 as that of its oxide.

*Chloride of bismuth.*—The solution of bismuth in muriatic acid, being deprived of water by evaporation, yields a salt which is capable of being sublimed, and which deliquesces into what has been called *butter of bismuth*. A similar product is obtained by introducing finely divided bismuth into chlorine gas, when the metal takes fire and burns with a pale blue light. This compound is the only known *chloride of bismuth*. It was analysed by Dr. Davy, and found to contain

Bismuth	..... 66.4	..... 100.
Chlorine	..... 33.6	..... 50.6
	100.	

From this analysis, the equivalent of bismuth appears very nearly to agree with the number which is derived from the synthesis of the oxide.

*Iodide of bismuth* may be formed by heating that metal with iodine. It is of an orange colour and insoluble in water. With hydriodic acid, or hydriodate of potassa, nitrate of bismuth affords a deep chocolate-coloured precipitate.

*Salts of bismuth.*—*Sulphuric acid* acts when hot and concentrated on bismuth, and sulphurous acid is disengaged. A

part of the bismuth is dissolved; and the remainder is changed into an insoluble oxide. The sulphate, on the authority of Lagerhjelm, is stated to consist of

Oxide of bismuth . . .	66.353	. . . .	100.	. . . .	80
Sulphuric acid . . . .	33.647	. . . .	50.71	. . . .	40
	100.				120

Beside the neutral sulphate, Berzelius describes a subsulphate consisting of

					Atoms.
Oxide of bismuth . . . .	85.5	. . . . .	100	. . . . .	3
Sulphuric acid . . . . .	14.5	. . . . .	17	. . . . .	1
	100.				

*Nitric acid* dissolves bismuth with great rapidity. To one ounce and a half of nitric acid, diluted with half its weight of water, add, at distant intervals, one ounce of bismuth, broken into small pieces. The solution, when poured into water, shoots into fine transparent crystals, having the shape of oblique rhombs, and constituted of 1 atom of acid, 1 atom of base, and 3 atoms of water. When the nitric solution is added to water, it is decomposed, and a white substance is precipitated, which is the pigment called *magistery of bismuth* or *pearl-white*. This compound consists of hydrated oxide of bismuth united with nitric acid; and the supernatant liquid contains a solution of bismuth, with great excess of acid. The precipitate is soluble to a considerable extent in pure ammonia, and, according to Laugier, in carbonate of ammonia, but not so much so in pure fixed alkalis, or their carbonates. It is liable to be turned black by sulphureted hydrogen, and, by the vapours of putrefying substances in general. It is employed in medicine as a tonic, under the name of *subnitrate of bismuth*.

With *tartaric acid*, bismuth forms an insoluble salt; but, if this compound be boiled with tartrate of soda, or if supertartrate of soda be boiled with oxide of bismuth, a solution is obtained which is perfectly neutral, and holds much bismuth in combination. This solution is not precipitated, either by alkalis or alkaline carbonates, but is decomposed by hydrosulphuret of ammonia. When evaporated, it becomes adhesive like gum. Tartrate of bismuth and tartrate of potassa, also, form a soluble and neutral triple salt.

Bismuth may be made the basis of a sympathetic ink. The

acid, employed for this purpose, must be one that does not act on paper, such as the acetic. Characters, written with this solution, become black when exposed to sulphureted hydrogen.

*Sulphuret.*—Bismuth combines with sulphur, and forms a bluish grey sulphuret, having a metallic lustre, which is also found native. Lagerhjelm has analyzed it, and found it to consist of

Bismuth . . . . .	81.619 . . . . .	100
Sulphur . . . . .	18.381 . . . . .	22.52
		100.

Dr. Thomson found that 9 grains of pure bismuth converted into a sulphuret became 11 grains: hence the sulphuret is constituted of

Bismuth . . . . .	81.82 . . . . .	or 1 atom	72
Sulphur . . . . .	18.18 . . . . .	or 1 atom	16
			88
	100.		

*Alloys.*—Bismuth is capable of being alloyed with most of the metals, and forms with some of them compounds of remarkable fusibility. One of these is Sir Isaac Newton's *fusible metal*. It consists of eight parts of bismuth, five of lead, and three of tin, or, according to Döbereiner, when made in the best proportions, it is a compound of 1 atom of lead, 1 of tin, and 2 atoms of bismuth, or of an atom of the binary alloy of bismuth and lead, united to an atom of the binary alloy of bismuth and tin. (Ann. of Phil. N. S. ix. 389.) When thrown into water, it melts before the water is heated to the boiling point. But a more extraordinary compound was formed by Döbereiner, by mixing together 207 parts of lead, 118 of tin, 284 of bismuth, and 1617 of mercury, at the temperature of 64° Fahr. The thermometer descended 50°, viz. to 14° Fahr. It is from the property of forming fusible alloys, that bismuth enters into the composition of several of the *soft solders*, which, indeed, is its principal use in the arts.

Laugier effects the analysis of alloys of tin, lead, and bismuth, as follows. Dilute nitric acid oxidizes the tin, and the lead and bismuth are dissolved. Into the solution, he pours carbonate of ammonia, which at first throws down carbonates of lead and bismuth; but, being added in considerable excess, redissolves that of bismuth only. The carbonate of lead is next

washed on the filter with a solution of carbonate of ammonia, in order to remove any adhering carbonate of bismuth; and afterwards with warm water. To the alkaline liquid, neutralized by an acid, pure ammonia is added in excess. All the oxide of bismuth is precipitated, and, after being washed on a filter, is to be dried and weighed. (Phil. Mag. March 1828.)

Bismuth has the singular property of depriving gold of its ductility; even when combined with it in very minute proportion. This effect is produced by merely keeping gold in fusion near melted bismuth. It has, nevertheless, been employed by Chaudet in cupellation. (Ann. de Ch. et de Ph. viii. 113.)

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## SECTION XXX.

### *Copper.*

Copper, as it is found in commerce, is always contaminated with a little charcoal and sulphur, amounting to about one half of a grain in 100 grains. Lead, antimony, and arsenic, are also occasionally found in it (Phil. Mag. xlvii. 206.); and, in one instance, a very minute proportion of bismuth was found in copper of inferior quality. (Phillips, in Phil. Mag. March 1828.) The copper, to which the epithet *micaceous* has been given, owes that appearance to a crystallized scoria diffused through it. (Ann. de Ch. et de Ph. xxxiii. 327.) To fit copper for purposes of accuracy, it may be dissolved in dilute nitric acid; and, after adding water, may be precipitated from the solution by a polished plate of iron. The metal thus obtained should be washed, first with diluted acid, and then with water, and may either be fused, or kept in a divided form, which has been observed to be that of very thin flexible plates, and sometimes of crystals. (Ann. de Ch. et de Ph. xxxi. 100.)

Copper is a metal of a beautiful red colour, and admits of a considerable degree of lustre. Its specific gravity varies with the operations to which it has been subjected. Lewis states it at 8.830; Mr. Hatchett found that of the finest granulated Swedish copper to be 8.895; and Cronstedt states the specific gravity of Japan copper at 9, while Dr. Thomson, from his own experiments, makes it only 8.434.

Copper has considerable malleability, and may be hammered

into very thin leaves. It is, also, very ductile; and may be drawn into wire, which has great tenacity. At 27° Wedgwood, it fuses, and, by a sufficient increase and continuance of the heat, it evaporates in visible fumes.

*Oxides of copper.*—1. Copper is oxidized by air. This may be shown by heating one end of a polished bar of copper, which will exhibit various shades of colour, according to the intensity of the heat. A plate of copper, also, exposed for some time to heat, becomes covered with scales, which break off when the copper is hammered. They are composed of 62 of the black oxide and 38 copper. This imperfect oxide, when exposed on a muffle, is farther oxidized, and assumes a deep red hue. Copper is also oxidized by long exposure to a humid atmosphere, and assumes a green colour; but the green compound holds carbonic acid in combination. The oxides of copper do not return to a metallic state by the mere application of heat; but require, for their reduction, the admixture of inflammable matter. Copper does not decompose water, which may even be transmitted, in vapour, through a red hot tube of this metal, without decomposition.

Copper is susceptible of only two degrees of oxidizement; in its lower stage the compound is red; when oxidated to the maximum, it is black.

The *black* or *peroxide* may be obtained, either by calcining the scales of copper, which have already been alluded to, under a muffle; or, by decomposing nitrate of copper by carbonate of potassa, and igniting the precipitate; or by the simple ignition of the nitrate. It is composed, according to Proust, of

Copper . . . . .	80	. . . . .	100	. . . . .	64 = 1 atom.
Oxygen . . . . .	20	. . . . .	25	. . . . .	16 = 2 atoms.
	100				At. wt. 80

Berzelius, after examining the composition of this oxide, proposes only a very small change in the statement of Proust, *viz.* that 100 parts of copper unite with 25.272 oxygen to form the peroxide. (Ann. de Ch. et de Phys. xvii. 26.)

When to a solution of the nitrate, or of almost any other salt of copper, a solution of potassa is added, a blue precipitate appears, which is a combination of peroxide of copper with water, or a *hydrated peroxide of copper*. Collected on a filter, and dried at a very moderate heat, it shrinks like alumina, but



still retains its colour. At a higher temperature, the water is expelled, and about 75 parts of peroxide of copper are left by every 100. It is probably, therefore, a compound of 1 atom of peroxide with 3 atoms of water.

To prepare the *protoxide of copper*, Mr. Chevenix recommends the following process: Mix together  $57\frac{1}{2}$  parts of peroxide of copper, and 50 parts of metallic copper precipitated from the sulphate on an iron plate. Triturate in a mortar, and put the mixture, with 400 parts of muriatic acid, into a phial, which is to be well stopped. The copper and its oxide will be dissolved with heat. When potassa is poured into this solution, the oxide (or rather hydrated protoxide) of copper is precipitated of an orange colour. This oxide, when deprived of water, becomes red; but it attracts oxygen so strongly, that it can scarcely be dried without absorbing more. It is composed of

Copper	....	88.89	....	100.	....	64	= 1 atom.
Oxygen	....	11.11	....	12.5	....	8	= 1 atom.
				100.		At. wt. 72	

*Chlorides of copper*.—By the combustion of copper in chlorine gas two compounds are produced at the same time, one of which is a fixed easily fusible substance, resembling common rosin, and called by Boyle, who has described it, *rosin of copper*. It may be procured, also, by carefully evaporating and fusing the protomuriate; and it remains in the retort, after distilling a mixture of 2 parts of corrosive sublimate and 1 of copper filings. It is insoluble in water, but soluble in muriatic acid. Its colour is generally dark brown, but, if exposed to the air, it becomes green, or, if fused and slowly cooled, yellow and semi-transparent. It consists of

Copper	.....	64	.....	100
Chlorine	.....	36	.....	56
				100

Being constituted of an atom of each of its elements, it may be called the *protochloride of copper*. In this instance, precisely the same equivalent for copper is deducible from the protochloride, as from the protoxide.

The *perchloride of copper* may be formed by evaporating the solution of peroxide in muriatic acid, at a heat below 400° Fahr. Its colour is yellow, but, when dissolved in water,

which readily acts upon it, it affords a green solution, identical with the permuriate. It consists of

Copper	..... 60	..... 47	..... 100
Chlorine	.... 67	..... 53	..... 112
	127	100	

### *Salts of Copper.*

*Muriates of copper.*—Corresponding with the two chlorides of copper, we have also a *protomuriate* and *permuriate*. The latter is obtained by dissolving peroxide of copper in muriatic acid. By careful evaporation and cooling, the permuriate crystallizes in rhomboidal prismatic parallelpipeds, which are deliquescent and readily soluble both in water and alcohol. It is composed, according to Proust, of

Peroxide of copper	..... 40
Muriatic acid	..... 24
Water	..... 36
	100

The nearest atomic constitution to these proportions is that of 2 atoms of muriatic acid, 1 atom of base, and 6 of water, which would make the salt a *bi-permuriate of copper*.

Plates of copper, exposed to the vapour of muriatic acid, become covered with an insoluble coating of a green powder, which is, most probably, a true *muriate*, or compound of 1 atom of base + 1 atom of acid. It dissolves readily in muriatic acid, and, by the addition of alkalis, yields peroxide of copper.

By digesting a solution of permuriate of copper with filings of that metal, or by digesting 4 parts of peroxide and 5 of precipitated copper (copper separated from its solutions by a plate of zinc) we obtain a *muriate of protoxide* or *protomuriate*, the fresh portion of copper being oxidized at the expence of that which was held in solution. This salt is decomposed by merely pouring it into water. Alkalis throw down an orange-coloured precipitate. It consists, according to Proust, of

Copper	..... 65.80	{ forming } { protoxide }	73.88
Oxygen	..... 8.08		
Muriatic acid	..... 26.12		
			100.

The native green copper sand of Chili and Peru has been analyzed by Dr. John Davy, and found to be a compound of

Peroxide of copper .....	73.
Muriatic acid .....	16.2
Water .....	10.8
	<hr/>
	100.

Neither of the two last compounds agrees with the law of atomic proportions; but the green sand approaches nearly to a *submuriate*, consisting of one atom muriatic acid + 2 atoms of peroxide + 3 atoms of water.

It is a submuriate of copper that is formed by the destructive action of sea-water upon the copper sheathing of ships, the oxygen necessary to the formation of the muriate being derived from the air of the atmosphere. Now, according to the views of Sir H. Davy, copper can only act upon sea-water when in a positive state, and that philosopher was therefore led to conceive that, if the electric state of the copper were reversed, by bringing it into contact with some metal of more energetic electrical power, the action of the sea-water would cease. (Phil. Trans. 1824.) This led him to a discovery which promises to be most important in its practical consequences, *viz.* that extensive surfaces of copper may be completely protected from the corroding effects of sea water, by placing comparatively small quantities of malleable or cast iron in contact with the copper sheathing of a ship; and it has been found that the covering of vessels so protected is uninjured even by long voyages in tropical regions. This discovery has been applied by Dr. Bostock to the protection of utensils employed for culinary purposes. (Ann. of Phil. N.S. viii. 176.)

*Chlorate of copper* was formed by Vauquelin, by dissolving peroxide of copper in chloric acid. It is a bluish green salt, deliquescent, and difficultly crystallizable.

*Iodate of copper* is an insoluble substance. It is precipitated from solutions of copper by alkaline iodates.

*Nitrate of copper*.—Copper readily dissolves in nitric acid diluted with two or three parts of water, and nitrous gas, holding a little copper in solution, is evolved in great abundance. The solution at first is green and muddy, but by

degrees it becomes transparent and blue, and gives prismatic crystals of a fine blue colour, consisting, exclusive of water, of

Peroxide .....	42.61
Nitric acid .....	57.39

---

100.

Nitrate of copper is partly but not entirely decomposed by alkaline carbonates; for, after their full effect, Berzelius found that a precipitate is still occasioned by adding water impregnated with sulphureted hydrogen.

*A sub-nitrate of copper* is also described by Berzelius (82 Ann. de Ch. 250.) It may be obtained, either by adding a small portion of potassa or ammonia to the solution of the nitrate, or by heating the dry salt gently. It consists of

Peroxide of copper .....	66.
Nitric acid .....	18.9
Water .....	15.1

---

100.

These proportions are not very remote from 1 atom of acid + 4 atoms of peroxide + 8 of water.

*Ammoniuret of copper.*—Copper and its oxides are soluble in ammonia. The watery solution of ammonia, at its boiling temperature, acts rapidly on copper. (Mac Culloch.) Dry ammoniacal gas appears also to combine with heated copper. (Quart. Journ. xxix. 158.) If ammonia be added in excess to nitrate of copper, the precipitate which is first formed is re-dissolved. On this property depends the method of separating oxide of copper from other metallic oxides; from those of iron, for instance, which are not soluble by ammonia.

Peroxide of copper, digested in ammonia, forms a bright blue liquid; from which, by careful evaporation, fine blue crystals may be obtained, called ammoniuret of copper. Protoxide of copper also dissolves in ammonia, and yields a colourless solution, which becomes blue by exposure to the air, in consequence of the absorption of oxygen.

*Sulphates.*—Copper combines with strong sulphuric acid, at a boiling heat, and affords a blue salt, called *sulphate of copper*. In this process, part of the sulphuric acid is decomposed, and furnishes oxygen to the metal which is dissolved. It is there-

fore better, in preparing sulphate of copper, to use the oxide obtained by calcining copper scales with free access of air.

Sulphate of copper is a regularly crystallized salt, of a fine rich blue colour, soluble in four parts of water at 60°. The solution is decomposed by pure and carbonated alkalis. The former, however, re-dissolve the precipitate. Thus, on adding pure liquid ammonia to a solution of sulphate of copper, a precipitate appears, which, on a farther addition of the alkali, is re-dissolved, and affords a beautiful bright blue solution. The sulphate of copper is decomposed also by iron. If in a solution of this salt we immerse a polished plate of iron, the iron will soon acquire a covering of metallic copper. The crystallized salt gives up its acid on the application of heat, without decomposition; and an oxide of copper remains in the retort. The crystals are composed, according to Proust, with whose analysis a recent one by Dr. Thomson exactly agrees, of

Copper 25.6	}	forming black oxide	} 32	.. or 1 atom = 80
Oxygen 6.4				
Sulphuric acid . . . . .			32	.. or 2 atoms = 80
Water . . . . .			36	.. or 10 atoms = 90
			100	250

Exclusive of water of crystallization, Berzelius (77 Ann. de Ch.), from his own analysis, states its composition at

Peroxide of copper ..	50.90	.. 103.66	.. 1 atom	80
Sulphuric acid ....	49.10	.. 100.	.. 2 atoms	80
		100.		160

Strictly speaking, therefore, this salt is a *bi-sulphate*, a name which sufficiently designates it, and is preferable to that of *bi-persulphate*.

Proust described a *subsulphate of copper*, formed by adding solution of potassa to a solution of the above sulphate. Berzelius prepared it by the cautious addition of ammonia, and found it, on analysis, to be composed of

Peroxide of copper ..	80	.. 100	.. 2 atoms =	160
Sulphuric acid ....	20	.. 25	.. 1 atom =	40
		100	Atomic weight . . . .	200

Dr. Thomson has described, also, a *quadri-sulphate*, consisting of 1 atom of base + 4 atoms of acid. (Ann. of Phil. N. S. i. 244.)

No sulphate of the protoxide is yet known; for when sulphuric acid is brought into contact with the protoxide, one-half of the oxide gives up its oxygen to the other half, which thus becomes peroxide, and unites with the sulphuric acid. It is on this principle that Clement explains the spontaneous deposit of metallic copper from a solution of the sulphate, long kept in a wooden cistern. In this case the protoxide was probably formed by the action of gases disengaged from the wood. (See Ann. de Ch. et de Ph. Dec. 1824, p. 440, and Jan. 1826, p. 100.)

*Sulphite of copper* may be obtained by transmitting a current of sulphurous acid gas (which has been first passed through a small quantity of water, in order to deprive it of sulphuric acid) into a vessel containing water and peroxide of copper. A green liquid is formed, which contains sulphite of copper, with a large excess of acid; and sulphite of copper, in very small red crystals, remains at the bottom of the vessel. This salt has been investigated by Chevreul (83 Ann. de Ch. 181), and found to consist of

Protoxide of copper . . . . .	63.84
Sulphurous acid . . . . .	36.16
	<hr style="width: 100%;"/>
	100.

Copper exposed to a damp air rusts, and becomes covered with *carbonate of copper*. The same compound is still more readily produced by adding carbonated alkalis to the solutions of copper. The nitrate of copper, precipitated by carbonate of lime, affords a blue precipitate, called *Verditer*. This substance is nearly allied to the native blue carbonate in the nature and proportion of its ingredients. (Quart. Journ. iv. 279.) Verditer consists of

Water . . . . .	5.9
Carbonic acid . . . . .	24.1
Peroxide of copper . . . . .	67.6
Moisture and impurities . . . . .	2.4
	<hr style="width: 100%;"/>
	100.

Carbonate of copper, according to Gay Lussac, is decomposed by being boiled with water a sufficient length of time, and a black anhydrous oxide remains. (An. de Ch. &c. xxxvii. 335.) Acetate of copper, he asserts, undergoes a similar change by the action of boiling water.

Berzelius observes that sub-carbonate of copper differs greatly in appearance, when precipitated from a cold and from a hot solution. In the latter case, its colour is yellowish green; in the former, it is bluish green, and much more bulky. It is composed of

Peroxide of copper . . . .	71.7	.. 1 atom	.. 80
Carbonic acid . . . . .	19.7	.. 1 atom	.. 22
Water . . . . .	8.6	.. 1 atom	.. 9
	100.		111

From the analysis of Mr. R. Phillips, this appears also to be very nearly the composition of the native green carbonate of copper (malachite) which he found to consist of 72.2 peroxide, 18.5 acid, and 9.3 water.

*Phosphoric acid* unites with peroxide of copper in two proportions. If solutions of phosphate of soda and sulphate of copper be mingled together, a bluish green precipitate is formed, consisting of

1 atom of peroxide of copper . . . . .	80	. . . .	55.35
2 atoms of phosphoric acid . . . . .	56	. . . .	38.40
1 atom of water . . . . .	9	. . . .	6.25
	145		100.

It is therefore a *bi-phosphate*. The *phosphate* has not yet been formed artificially, but it has been found native in a white quartz rock. (Ann. of Phil. N. S. iii. 182.) It is of an emerald green colour, and is not crystallized. Its analysis afforded results very nearly agreeing with

1 atom of peroxide of copper . . . . .	80	. . . .	63.59
1 atom of phosphoric acid . . . . .	28	. . . .	22.03
2 atoms of water . . . . .	18	. . . .	14.38
	126		100.

When corroded by long continued exposure to the fumes of *acetic acid*, copper is converted into verdigris. The verdigris of commerce is composed partly of a salt, soluble in water, and partly of a light green powder, which is not soluble in water. By the solution of verdigris in distilled vinegar, and evaporation, a salt is obtained in regular crystals. These crystals have been analyzed by Mr. Richard Phillips, and shown to consist of

2 atoms of acetic acid ..	$50 \times 2 = 100$	.. or 50.11
1 atom of peroxide of copper ....	$= 80$	.... 37.77
3 atoms of water .....	$9 \times 3 = 27$	.... 12.12
	$207$	$100.$

A previous analysis by Dr. Ure had already given the same results, except in assigning 2 atoms only of water, and a different equivalent for acetic acid; and Berzelius's subsequent analysis agrees with the latter proportions. All concur to show that the salt is strictly a *binacetate*, and by that name it is proper to designate it. (Ann. of Phil. N. S. i. 418, ii. 21, iv. 161, and viii. 188.) If it contain only 2 atoms of water, it will be constituted as follows:

Acetic acid, 2 atoms ....	$100$	.. or 51.22
Peroxide .. 1 atom ....	$80$	.... 39.76
Water . . . 2 atoms .....	$18$	.... 9.02
	$198$	$100.$

*Binacetate of copper* forms large and beautiful crystals, the primary form of which is an oblique rhombic prism. (Ann. of Phil. vi. 39.) It is soluble in twenty parts of water at  $60^\circ$ , or in five parts at  $212^\circ$ . When distilled *per se*, it yields concentrated acetic acid, which may be purified by a second distillation; and in the retort a compound is left of charcoal and oxide of copper, which sometimes kindles spontaneously like pyrophorus. When this substance is calcined with free access of air, it becomes *peroxide*.

*Verdigris*, from the experiments of Mr. Phillips, with which those of Berzelius agree, appears to consist essentially of very minute blue crystals, which are composed of

Acetic acid . . . . .	$28.30$	.... 1 atom .... 50
Peroxide . . . . .	$43.25$	.... 1 atom .... 80
Water . . . . .	$28.45$	.... 6 atoms .... 54
	$100.$	$184$

In verdigris, when dried for sale, the same relative proportion of acid and base exists, but the water is reduced to twenty-five parts, or a little more, in 100; and there is a quantity of insoluble impurity varying from 0.5 to 2 per cent.

The blue crystals found in verdigris are, therefore, a true *acetate of copper*, consisting of an atom of acid + 1 atom of



peroxide. When acted upon by water, they are decomposed; a green insoluble powder is obtained, which is a real *subacetate*, constituted of 1 atom of acid + 2 of peroxide. The blue solution contains a binacetate. Three distinct compounds, therefore, exist of acetic acid and peroxide of copper; the subacetate, acetate, and binacetate.

The subacetate is constituted of 1 atom acid + 2 base.  
 acetate ..... 1 atom acid + 1 base.  
 binacetate ..... 2 atoms acid + 1 base.

In an elaborate memoir on the combinations of acetic acid with peroxide of copper, (Ann. of Phil. N. S. viii. 188,) Berzelius describes three additional compounds, two of which are produced by the action of distilled water on verdigris. One of these is a subsalt, soluble in water, consisting of

	By expt.	By calc.	
Acetic acid . . . . .	36.80	37.14	.. or 4 atoms
Peroxide of copper	43.19	43.24	.... 3 atoms
Water . . . . .	20.01	19.62	.... 12 atoms
	100.	100.	

It may be considered, therefore, as a *subsesquacetate*. The second, an insoluble salt, is obtained by allowing verdigris to swell in water, and afterwards filtering it through coarse linen, which allows minute scaly crystals to pass through. They are constituted of

	By expt.	By calc.	
Acetic acid . . . . .	27.60	27.83	.. or 2 atoms
Peroxide . . . . .	64.36	64.82	.... 3 atoms
Water . . . . .	8.04	7.35	.... 3 atoms
	100.	100.	

When a dilute solution of the soluble subsalt is heated, it deposits a flocculent liver-brown coloured substance, which, collected upon a filter, appears black. It is composed of

	By expt.	By calc.	
Acetic acid . . . . .	2.45	2.44	.. or 1 atom
Peroxide . . . . .	92.	92.30	.... 24 atoms
Water . . . . .	5.55	5.26	.... 12 atoms
	100.	100.	

When the muriate of copper is mixed with a solution of ferrocyanate of potassa or of lime, a beautiful reddish brown preci-

pitate of *ferro-cyanate of copper* is obtained, which has been recommended by Mr. Hatchett as a pigment. Tincture of galls throws down, from all the solutions of copper, a dull yellow precipitate.

*Sulphurets.*—Copper combines with sulphur in two proportions. When a mixture of three parts of the metal, in the state of fine filings, with one part of sulphur, is melted in a glass tube, at the moment of combination, a brilliant inflammation ensues, exceeding in brightness that produced by the fusion of iron and sulphur.

Copper leaf, Berzelius observes (79 Ann. de Ch. 250,) burns in gaseous sulphur as brilliantly as iron wire in oxygen gas. A compound is formed, precisely analogous to the native black sulphuret of copper, or *copper glance*. It is a *proto-sulphuret*, and consists of

Copper	.....	80	....	100	.. or 1 atom =	64
Sulphur	.....	20	....	25	.... 1 atom =	16
		100		125		80

Beside this, there is also a *per-sulphuret* or *bi-sulphuret*, which is the principal ingredient of yellow copper pyrites, and from the observations of Covelli, (An. de Ch. &c. May 1827,) appears to be constantly forming in the crater of Vesuvius. It may also be produced, artificially, by rubbing the sulphuret, finely powdered, with strong and pure nitric acid at common temperatures. The bi-sulphuret thus formed is a greenish black powder. (Faraday, Quart. Journ. xxi. 183.) It is also produced when we act with sulphureted hydrogen on a per-salt of copper. It consists of

Copper	....	66.66	....	100	.. or 1 atom =	64
Sulphur	....	33.34	....	50	.... 2 atoms =	32
		100.				96

Copper unites by fusion with *phosphorus*. The phosphuret is white, brittle, and of the specific gravity 7.122. The analysis of Pelletier gives 20 of phosphorus to 100 metal, which nearly agrees with 1 atom of phosphorus + 1 atom of copper."

*Atomic weight of copper.*—Two views have been taken of the atomic weight of copper; for we may consider the compound of that metal with the smallest proportion of oxygen, not as the protoxide, but as a suboxide, that is, as consisting of 2 atoms of

metal to 1 of oxygen, in which case the black oxide will be the true binary compound, and not the ternary one, as it has been represented in this section. On this supposition, which has been adopted by Drs. Wollaston, Prout, and Thomson, the atom of copper will be represented by 32 instead of 64. This certainly does away with an anomaly, occasioned by adopting 64 as its relative weight, *viz.* that all the salts of copper are bisalts, or contain 2 atoms of acid united to 1 of base. But, on the other hand, it is singular that the compounds of copper with the smallest proportions of sulphur and of chlorine should contain 2 atoms of base, for in general these compounds agree with the compound containing least oxygen in being binary ones, and no good reason can be given why, in this instance, there should be a departure from the general law. It may be well, however, to exhibit a few of the changes which will be necessary, if 32 be adopted for the atomic weight of copper.

The *protoxide* must then be considered as a *suboxide*, constituted of 2 atoms of copper (64) + 1 atom of oxygen (8) giving 72 for its atomic weight.

The *peroxide*, as the true *oxide* of copper, consisting of 1 atom of copper (32) + 1 atom of oxygen, together = 40.

The *sulphuret* as a *disulphuret*, containing 2 atoms of copper (64) + 1 atom of sulphur (16), and its atomic weight as 80.

The *bisulphuret* as the true sulphuret, composed of 1 atom of copper (32) + 1 of sulphur (16) = 48.

The *protochloride* will be a *dichloride*, containing 2 atoms of copper (64) + 1 atom of chlorine (36), and its equivalent 100.

The *perchloride* will be the true *chloride*, containing 1 atom of copper (32) + 1 atom of chlorine (36), and its atomic weight 68.

The *bisulphate* will be the true *sulphate*, containing 1 atom of base (40) + 1 of acid (40) together 80, and the crystals will contain only 5 instead of 10 atoms of water, to preserve the same relative proportions of anhydrous sulphate and water.

The *binacetate* will be an *acetate*, containing 1 atom of base (40) + 1 atom of acetic acid (50), together 90. And so of the rest.

*Alloys.*—Copper combines readily with most of the metals, and affords several compounds, which are of great use in the common arts of life. *Chinese white copper* is an alloy of copper, zinc, iron, and nickel, obtained probably from a compound

ore of those metals. (Ann. of Phil. N. S. v. 236.) Copper, with about a fourth its weight of lead, forms *pot-metal*; with about the same proportion of zinc, or a little more, it composes *brass*, the most useful of all its alloys. Mixtures of zinc and copper form, also, the various compounds of *Tombac*, *Dutch Gold*, *Similor*, *Prince Rupert's Metal*, *Pinchbeck*, &c. Copper with tin, and sometimes a little zinc, forms *bronze* and *bell-metal*, or *gun-metal*. And when the tin is nearly one-third of the alloy, it is beautifully white, and takes a high polish. It is then called *speculum-metal*. (Nicholson's Journ. 4to. iii. 490.) Copper may also be alloyed with iron; but the compound has no useful properties. (49 Phil. Mag. 107.)

Respecting the alloys of copper, much valuable information may be found in the 4th volume of Bishop Watson's Chemical Essays, and in Aikin's Dictionary of Chemistry, articles *Brass*, &c. Mr. Dalton finds that into all the alloys of copper, which are characterized by useful properties, the ingredients enter in atomic proportions; and it is probable that, by attention to these proportions, the manufacture of the artificial alloys may be greatly improved.

Most of the copper of commerce is obtained from *copper pyrites*, or *yellow copper ore*, which is a compound of sulphur, iron, and copper, in such proportions, as render it probable that it is composed of 2 atoms of proto-sulphuret of iron, and 1 atom of per-sulphuret of copper with a little arsenic and earthy matter. (R. Phillips, Ann. of Phil. N. S. iii. 301.) The sulphur and arsenic are separated by roasting; and the copper is obtained by repeated fusions, in some of which an addition of charcoal is made.

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## SECTION XXXI.

### *Tellurium.*

Tellurium was discovered by Klaproth, in an ore of gold. (See his Contributions, ii. 1.) His process for extracting it consists in the solution of the ore by nitro-muriatic acid, dilution with water, and the addition of pure potassa, which throws down all the metals that are present; and, when added in excess, re-dissolves a white precipitate, which it at first occasions. To the alkaline solution, muriatic acid is then added; a precipitate

again appears; and this, when dried, and heated with one twelfth its weight of charcoal, or with a small quantity of oil, in a glass retort, yields tellurium, in the form of small brilliant metallic drops, lining the upper part of the body of the retort.—One hundred parts of the ore yield above 90 of tellurium.

The colour of this metal is tin-white, verging to lead-grey; it has considerable lustre, and a foliated, or scaly fracture. It is very brittle; is fusible at a temperature below ignition; and, excepting osmium and quicksilver, is the most volatile of all metals. It is also the lightest of the metals, the bases of the alkalis and earths excepted, having the specific gravity of only 6.185.

*Oxides.*—Tellurium is oxidized when heated in contact with air; and burns with a sky-blue flame, edged with green. Upon charcoal, before the blow-pipe, it inflames with a violence almost amounting to detonation; exhibits a vivid flame; and entirely flies off in a grey smoke, having a peculiarly nauseous smell. This smoke when condensed, and examined in quantity, is found to be white with a tint of yellow. It is fusible by a strong heat, and volatile at a still higher temperature. It not only unites as a base with acids, but also itself possesses the character of an acid, and forms a class of salts, which may be called *tellurates*. It is composed, according to Klaproth, of

Tellurium .....	83	.....	100.
Oxygen .....	17	.....	20.5
	<hr style="width: 50px; margin: 0 auto;"/>		
	100		

Berzelius, however, determines the quantity of oxygen, absorbed by 100 of tellurium, when changed into oxide, to be 24.8. If this result be correct, and the compound be the protoxide, the atom of tellurium should weigh 32, and the oxide 40.

Tellurium, moistened with concentrated sulphuric acid, is dissolved into a fluid perfectly transparent, of a fine crimson colour, without the disengagement of any gas or any sensible odour of sulphurous acid. On the addition of a due quantity of water, the tellurium is precipitated in form of a metallic powder, of a deep brown and almost black colour. Exposure of the crimson liquor to the contact of air causes the formation of a sulphate of oxidized tellurium. (Ann. Chim. et de Ph. xxxvii. 188.)

Tellurium is soluble in nitric and nitro-muriatic acids. The

saturated solution is decomposed by the mere addition of water, which throws down a white powder; but this is again dissolved on adding more water. Chlorine unites with tellurium, and forms a white semi-transparent compound, which is decomposed when added to water. It consists, according to Sir H. Davy, of 100 tellurium united with 90.5 chlorine. From its solutions, tellurium is precipitated in a metallic form, by iron, zinc, tin, and even by muriate of tin. Carbonated and pure alkalis precipitate the telluric oxide united with water, in the form of a white hydrate; and the oxide is re-dissolved by an excess of alkali or carbonate. Alkaline sulphurets throw down a dark brown or blackish precipitate. Tincture of galls produces a flocculent yellow precipitate. The solutions of this metal in acids are not decomposed by ferro-prussiate of potassa; a property which tellurium possesses in common with gold, platinum, iridium, osmium, rhodium, and antimony.

Tellurium forms two distinct compounds with hydrogen, the one of which is solid and the other gaseous. 1. By making tellurium the negative surface in water, in the Galvanic circuit, a brown powder is formed, which is a solid *hydruret of tellurium*. 2dly. By acting with dilute sulphuric acid, upon the alloy of tellurium and potassium (which may be obtained by heating a mixture of solid hydrate of potassa, tellurium, and charcoal,) we obtain a peculiar gas. This gas has a smell resembling that of sulphureted hydrogen. It is absorbed by water, and a claret-coloured solution results, which, by exposure to the air, becomes brown, and deposits tellurium. After being washed with a small quantity of water, it does not affect vegetable blue colours. It burns with a bluish flame, depositing oxide of tellurium. It unites with alkalis; precipitates most metallic solutions; and is instantly decomposed by chlorine gas. It may be called *tellureted hydrogen gas*. According to Berzelius, it is constituted of 100 parts of tellurium with a little less than two parts of hydrogen. It probably consists, Dr. Thomson thinks, of 1 volume of tellurium vapour and 1 volume of hydrogen gas condensed into 1 volume, which would give tellureted hydrogen the sp. gr. of 2.2916 and the atomic weight of 33.

## SECTION XXXII.

*Lead.*

To obtain lead in a state of purity, Berzelius dissolved it in nitric acid, and crystallized the salt several times, till the mother liquor, on adding carbonate of ammonia, gave no traces of copper. The pure nitrate of lead, mixed with charcoal, was strongly heated in a Hessian crucible; and the lead, which separated, was kept some time in a state of fusion, in order to free it entirely from charcoal. The lead, thus obtained, when redissolved in nitric acid, gave no trace of any other metal.

Lead has a bluish white colour; and, when recently cut or melted, exhibits considerable lustre, which soon, however, tarnishes. Its specific gravity is 11.352. Its malleability is sufficient to allow of its being beaten into very thin leaves; and it may be drawn into wire, which has less tenacity, however, than that of most other metals.

The melting point of lead, according to Morveau, is 590° Fahrenheit; but according to Mr. Crichton of Glasgow it is 612°. Exposed to a red heat, with free access of air, it smokes and sublimes, and gives a grey oxide, which collects on surrounding cold bodies. It is slowly oxidized, also, by exposure to the atmosphere at common temperatures; and more rapidly, when exposed alternately to the action of air and water.

*Oxides of Lead.*—Lead appears to be susceptible of forming three distinct oxides. 1. The *yellow protoxide* may be obtained by decomposing nitrate of lead with carbonate of soda, and igniting the precipitate, or by heating the nitrate to redness in a close vessel. This oxide is tasteless, insoluble in water, but soluble in potassa and in acids. When heated, it forms on cooling a yellow semi-transparent glass, called *litharge*, which is, to a considerable degree, volatile at a red heat, and has been obtained in regular crystals. (Phil. Mag. April 1827, p. 312.) Another form of the yellow oxide is that which is known in commerce by the name of *massicot*.

The yellow or *protoxide* of lead has been investigated by Proust, Thomson, and Berzelius. Its composition, as determined by the last-mentioned chemist, is

Lead . . . . .	92.85	. . . . .	100.	. . . . .	104
Oxygen . . . . .	7.15	. . . . .	7.725	. . . . .	8
	100.				112

2. The second, or *deutoxide* of lead, may be obtained by exposing the protoxide of lead, or the metal itself, to heat, with a large surface and a free access of air, for some time, till, at length, its is converted into a red oxide, known in commerce by the names of *minium* or *red lead*. This, however, is an impure substance, containing sulphate of lead, muriate of lead with excess of base, oxide of copper, silica, and a portion of the yellow oxide. The protoxide, Berzelius found, may be removed by acetic acid, which does not act on the red oxide. Making allowance for the other impurities, he determined the composition of red oxide of lead, which may be considered as the deutoxide, to be

Lead . . . . .	90	. . . . .	100.	. . . . .	104
Oxygen . . . . .	10	. . . . .	11.08	. . . . .	12
	100				116

Minium, however, is denied by Longchamp to be a peculiar oxide of lead, and is considered by him as a compound of 1 atom of puce-coloured oxide, with 1 atom of litharge (34 Ann. Ch. et Ph. 105.) From the analysis of a fine specimen of crystallized minium, M. Houton-Labillardiere deduces the protoxide to be to the tritoxide in that compound as 3 to 1, while Berzelius and Thomson find in it equal proportions, probably from having employed a less pure substance. (34 Ann. Ch. et Ph. xxxv. 97.) Mr. Dalton, from his own experiments, is disposed to regard minium as 1 atom of oxygen united with 6 atoms of protoxide. (N. Syst. ii. 47.)

When minium is digested with nitric acid, one part of it is reduced to the state of yellow oxide, and is dissolved by the acid; and the remainder is a brown oxide, contaminated (if impure minium has been used) with the substances which have been mentioned. This per-oxide may be procured, also, by passing a current of chlorine gas through water, in which the red oxide is kept suspended, and by precipitating clear solution with caustic potassa, and drying the oxide. It is of a flea or puce colour; very fine and light in its texture; and insoluble



in nitric acid. When strongly heated, it gives out 3 or 4 per cent. of oxygen gas, and is converted into yellow oxide. It consists, according to Berzelius, of

Lead	..... 86.51	.... 100	.... 104
Oxygen	..... 13.49	.... 15.6	.... 16
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.	115.6	120

On comparing the quantities of oxygen united with 100 parts of lead, in these three oxides, we shall find that the numbers 7.7, 11.08, and 15.6, are very nearly in the proportion of 1,  $1\frac{1}{2}$ , and 2. If, therefore, we multiply these last numbers by 2, we shall have the oxygen, in the three oxides of lead, represented by 2, 3, and 4. This view of the subject renders it probable, that there may exist an oxide of lead, with less oxygen than any at present known; but the notion is not countenanced by the composition of the sulphuret. From the protoxide, the weight of the atom of lead is determined to be 104, and the composition of the three oxides is as follows:

Protoxide 104 lead + 8 oxygen = 112

Deutoxide 104 lead + 12 oxygen = 116

Peroxide 104 lead + 16 oxygen = 120

The yellow oxide of lead, when precipitated by pure alkalis from its compounds, forms a white *hydrate*, the composition of which is not exactly known.

The oxides of lead are easily vitrified, and have the property of uniting with all the metals except gold and silver. Hence gold or silver may be purified by melting them with lead. The lead becomes first oxidized and then vitrified, and sinks into the cupel, carrying along with it all the baser metals, and leaving the gold or silver on the surface of the cupel. The quantity of lead required for silver of various degrees of fineness may be learned from a memoir of D'Arcet, in the first volume of *Annales de Chim. et de Physique*.

The oxides of lead give up part of their oxygen on the application of heat. When distilled in an earthen retort, they afford oxygen gas; and still more readily when acted upon by concentrated sulphuric acid. They are completely reduced, by being ignited with combustible matter. Thus, when a mixture of red oxide of lead and charcoal is ignited in a crucible, a button of metallic lead will be found at the bottom of the vessel. Mere trituration of the peroxide in a mortar with a little sulphur, and

the subsequent addition of a small bit of phosphorus, occasions a violent explosion. (Thomson's Annals, ix. 31.)

Pure water has no action on lead, but it takes up a small proportion of the oxide of that metal. When left in contact with water, with the access of atmospherical air, lead soon becomes oxidized and dissolved, especially if agitation be used. Hence the danger of leaden pipes and vessels for containing water, which is intended to be drunk. Water acts, also, more readily on lead, when impregnated with lime, or with the neutral salts that are occasionally present in spring water, and Dumas has rendered it extremely probable that galvanic electricity in that case has a great share in causing the action of salts on lead. Water, for instance, in which carbonate of lime is held in solution by carbonic acid, acts chiefly on those parts of leaden pipes or vessels that are united by solder. He proposes, therefore, to obviate this action by protectors formed on the same principle with those invented by Sir H. Davy for the bottoms of ships. (Ann. de Ch. et de Ph. xxxiii. 265.)\*

*Chloride of Lead.*—When 30 grains of lead, reduced to fine filings, are thrown into 60 cubic inches of chlorine gas moderately warmed, the metal burns with a clear white flame accompanied with sparks. The combination of lead and chlorine may, however, be more easily effected, by precipitating the nitrate or any soluble salt of lead with a solution of common salt, and washing the precipitate with a sufficient quantity of water. It has a sweet taste, and is soluble in 22 parts of water at 60°, and also in diluted nitric acid. When dry, it is fusible, at a heat below redness, into a semi-transparent substance of the consistence of horn, from whence it has been called *horn lead* or *plumbum corneum*. By an intense heat it is volatilized. It has been analyzed by Berzelius, who states it to consist of 100 muriatic acid + 409.06 protoxide of lead, equivalent to 380.06 metallic lead + 129 chlorine. Dr. John Davy found it to be composed of

Chlorine	..... 25.78	..... 34.75	..... 36
Lead	..... 74.22	..... 100.	..... 104
	100.		140

\* On the presence of lead in water, consult Dr. Lambe's "Researches respecting Spring Water," 8vo. London. Johnson) and also Guyton, 26 Nich Journ. 102.

It is the only compound of lead and chlorine that is known, and it is constituted of 1 atom of each of its elements.

When two parts of the red oxide of lead are made into a paste with one of chloride of sodium, and water added occasionally as the mixture hardens, soda is disengaged, and a *subchloride* of lead is formed mixed with oxide of lead. This, on fusion, affords the fine yellow pigment called *mineral or patent yellow*. The disengaged soda attracts carbonic acid from the atmosphere, but not enough to convert it into a carbonate. In the large way, it is found necessary to supply carbonic acid to the soda thus formed, by burning it with saw-dust. By this process, a large quantity of soda was extracted from common salt, till cheaper methods were discovered.

*Iodide of lead* may be prepared either by the direct combination of iodine with lead, or by precipitating nitrate of lead with hydriodic acid, and heating the precipitate. It is constituted of 1 atom of iodine = 125 + 1 atom of lead = 104, together 229.

*Iodate of lead* is thrown down in an insoluble state when iodate of potassa is added to nitrate of lead.

#### *Salts of Lead.*

*Sulphuric acid* has no action on lead, except when concentrated and at a boiling temperature. It is then decomposed, and sulphurous acid is formed. The insolubility of lead in sulphuric acid occasions its being employed as the material for constructing the chambers in which that acid is prepared, and even for boiling down the weak acid. Sulphate of lead, however, may be formed, either by adding sulphuric acid, or, still better, sulphate of soda, to any of the salts of lead. Though it is found native in regular crystals, it cannot be crystallized artificially. Its insolubility both in water and in nitric acid renders its formation of use as a step in mineral analyses, and hence it is necessary to know its exact composition, which is stated by Berzelius as follows:—

Sulphuric acid ..	26.34	....	100	....	1 atom =	40
Yellow oxide ....	73.66	....	279	....	1 do. =	112
	100.		379			152

*Sulphite of lead* may be formed by the direct action of sulphurous acid on the protoxide, or by mingling solutions of nitrate of lead and sulphite of potassa. It is white, insoluble, and

tasteless, and gives sulphurous acid when heated. It consists of 1 atom of base = 112 + 1 atom of acid = 32.

*Nitrate of lead.*—Nitric acid, a little diluted, dissolves lead, with the extrication of nitrous gas. If the acid be in small quantity, a *sub-nitrate* is formed, which becomes soluble on adding more acid. A small portion remains undissolved, which Dr. Thomson finds to be oxide of antimony with a little silica. The solution is not decomposed when poured into water. By evaporation, it yields large regular tetrahedral or octohedral crystals, which are soluble in about  $7\frac{1}{2}$  parts of boiling water. They contain no water of crystallization, and consist, according to Berzelius, of

Nitric acid . . . .	32.78	. . . . 100	.. 1 atom =	54
Yellow oxide ..	672.2	. . . . 209.5	.. 1 do. =	112
	100.	309.5		166

Chevreul erroneously considers this salt as a super-nitrate, (Thomson's Annals 101,) and describes a scaly salt as the neutral nitrate, in fact, which is a *sub-nitrate*, (*di-nitrate* of Thomson) consisting of

Nitric acid . . . . .	19.86	. . . . 100	.. 1 atom =	54
Yellow oxide . . . . .	80.14	. . . . 403	.. 2 do. =	224
	100.	503		278

By boiling 4 parts of the nitrate, and 6 of lead, with 350 parts of water, for 14 hours, Chevreul obtained a liquid, which yielded two sorts of crystals; the one, in the form of plates, a *nitrite*; and the other in the shape of needles, a *sub-nitrite* or *di-nitrite*. The nitrite was little soluble in cold water, and boiling water dissolved only about a tenth of its weight. It was decomposed by all the acids that were tried. Its constituents are

Nitrous acid . . . . .	18.15	. . . . . 100
Yellow oxide . . . . .	81.85	. . . . . 450

100.

The sub-nitrite crystallized in needles, of which 100 parts of boiling water dissolved about three parts, and retained one, when cooled down to  $73^{\circ}$  Fahr. It consisted of

Nitrous acid . . . . .	9.9	. . . . . 100
Yellow oxide . . . . .	90.1	. . . . . 910

100.

*Hyponitrite of lead.*—Berzelius obtained this salt by dissolving a given quantity of di-nitrite of lead in water, adding sufficient sulphuric acid to throw down half the lead, filtering the solution, and allowing it to crystallize spontaneously. The crystals consisted of

Hyponitrous acid . . . .	23.90	. . . .	or 1 atom ..	38
Protoxide of lead . . . .	70.44	. . . .	or 1 atom ..	112
Water . . . . .	5.66	. . . .	or 1 atom ..	9
	100.			159

*Carbonate of lead.*—Carbonic acid may be made to combine with protoxide of lead, by precipitating the nitrate with carbonate of soda, or by long exposure of thin sheets of lead to the vapour of vinegar. In the latter case, we obtain the carbonate of lead or common white lead, which Bergman has shown to contain no acetic acid, though made by its intervention. According to Berzelius it consists of

Carbonic acid ..	16.5	. . . .	100.	. . . .	1 atom =	22
Oxide of lead ..	83.5	. . . .	506.82	. . . .	1 atom =	112
	100.					134

*Acetate and sub-acetate.*—When carbonate of lead is dissolved in distilled vinegar, and the solution crystallized, we obtain a salt of great utility in the arts, the super-acetate, or more properly, acetate of lead, long known, from its sweet taste, under the name of *sugar of lead*.

It is in the form of small shining needle-shaped crystals, which are almost equally soluble in hot and in cold water, *viz.* to about one-fourth the weight of the fluid. The solution is decomposed by mere exposure to the air, the carbonic acid attracting the lead, and forming an insoluble carbonate. It is decomposed, also, by the carbonates and sulphates of alkalis.

Acetate of lead consists, according to the experiments of Berzelius, of

Acid . . . . .	26.97	. . . .	100.	. . . .	1 atom ..	50
Yellow oxide	53.71	. . . .	217.662	. . . .	1 ditto ..	112
Water . . . .	14.32	. . . . . 3 ditto ..				27
	100.					189

By boiling in water a solution of 100 parts of acetate of lead and 150 of finely pulverized litharge, the acetate passes to the

state of *sub-acetate*. The taste of this salt is less sweet; it is less soluble in water, and crystallizes in plates. It is composed, according to Berzelius, of

Acid . . . . .	13.23	. . . .	100	. . . .	1 atom	..	50
Yellow oxide . . .	86.77	. . . .	656	. . . .	3 ditto	..	336
<hr style="width: 20%; margin: 0 auto;"/>							
100.							

This salt is called by Dr. Thomson the *trisacetate*, and he has described also a *diacetate* or compound of 2 atoms of base with 1 atom of acid, and 10 of water, formed by boiling crystals of acetate of lead and litharge, in proper proportions, with the requisite quantity of water. (First Prin. ii. 373.)

*Phosphate of lead*.—The yellow oxide of lead unites with phosphoric acid, either directly, or by mixing the solutions of a neutral alkaline phosphate and of nitrate or acetate of lead. The compound is insoluble, and is composed, according to Dr. Thomson, (Ann. of Phil. i. 12.) of

Phosphoric acid ..	20	. . . .	100	. . . .	1 atom =	28
Yellow oxide . . . . .	80	. . . .	400	. . . .	1 ditto =	112
<hr style="width: 20%; margin: 0 auto;"/>						
	100		500			<hr style="width: 20%; margin: 0 auto;"/>
						140

There is also, according to Dr. Thomson, a *di-phosphate*, consisting of 1 atom of phosphoric acid, and 2 atoms of the protoxide.

*Chromate of lead* is found native in fine orange-coloured prisms. It is anhydrous, and is constituted of

Chromic acid . . . . .	1 atom	52
Protoxide of lead . . . . .	1 ditto	112
<hr style="width: 20%; margin: 0 auto;"/>		
164		

*Sulphuret of lead*.—All the solutions of lead are decomposed by sulphureted hydrogen and by alkaline hydro-sulphurets, and a hydro-sulphureted oxide is thrown down. Hence these compounds are excellent tests of the presence of lead in wine or any other liquor, discovering it by a dark-coloured precipitate. Hence, also, characters traced with solution of acetate of lead become legible when exposed to sulphureted hydrogen gas. The same property explains, too, the effect of alkaline hydro-sulphurets in blackening the glass bottles in which their solutions are kept. The effect is owing to the action of the sulphureted hydrogen on the oxide of lead which all flint glass contains.

Lead unites also in its metallic state with sulphur; and constitutes a native compound of a blue colour with considerable brilliancy called *galena*, which is the source of almost all the lead of commerce. This compound may, also, be formed artificially. The sulphur and lead, which it contains, are in such proportions, that when both are combined with oxygen, and converted, the one into sulphuric acid, and the other into yellow oxide of lead, the acid and oxide exactly saturate each other. These proportions are,

Sulphur	....	13.36	....	or 1 atom	16
Lead	.....	86.64	....	or 1 atom	104

Weight of its atom .. 120

The decomposition of sulphuret of lead by carbonate of soda, jointly with charcoal, and the formation of double sulphurets, have been investigated by Berthier, in a memoir of great interest to all who are concerned in metallurgical operations. (*Ann de Ch. et de Ph.* xxxiii. 154.)

The alloys of lead are described in other sections of this chapter.

## CLASS II.

METALS, THE OXIDES OF WHICH ARE REDUCIBLE BY  
HEAT ALONE.

## SECTION XXXIII.

*Mercury.*

MERCURY, or quicksilver, is the only one of the metals that retains a fluid form at the ordinary temperature of the atmosphere. When, however, it is reduced to about  $39^{\circ}$  or  $40^{\circ}$  below zero of Fahrenheit, it becomes a solid, which may be flattened with a hammer, or cut with a knife. This is a degree of cold, however, that occurs in few climates. In this country, quicksilver can only be exhibited in a solid state by means of artificial mixtures. By congelation it acquires an increase of specific gravity; and, therefore, unlike other metals, the congealed portion sinks to the bottom of a fluid mass of mercury. Its specific gravity, at  $47^{\circ}$  above 0 of Fahrenheit, being 13.545, it was found increased by congelation, in an experiment of Mr. Biddle, to 15.612, or about one-seventh.

At about  $660^{\circ}$  of Fahr.,  $656^{\circ}$  according to Crichton,  $680^{\circ}$  according to Petit and Dulong, or  $662^{\circ}$ , measured by a true thermometer, mercury boils, and is changed into vapour. Hence it may be driven over by distillation, and may thus be purified, though not accurately, from the admixture of other metals. When its temperature is considerably increased above this point, the vapour acquires great expansive force, and the power of bursting the strongest vessels.

Gay Lussac calculated that the vapour of mercury is 12.01 times more dense than oxygen gas, and that the liquid metal, in becoming gaseous, increases in volume 961 times. Dumas, by actually weighing its vapour, finds its specific gravity, compared with that of air, to be 6.9760. (An. de Ch. et de Ph. xxxiii. 353.) The evaporation of quicksilver *in vacuo* at common temperatures is shown by the fact, that in warm weather mercurial vapour forms spontaneously in the upper part of a barometer tube, and condenses in minute drops on its inner surface.



It has been supposed that mercury has the property of containing air within its pores, in the same invisible state in which air exists in water; but it appears probable, from the remarks of Mr. Daniel, that the air which escapes, on boiling mercury in a glass vessel, arises only from the surface of the glass, with which it is retained in contact. (Met. Essays, p. 363.)

#### *Oxides of Mercury.*

Mercury is not oxidized, when pure, at the ordinary temperature of the atmosphere; but preserves the lustre of its surface unchanged for a considerable time. There are several methods, however, by which it may be brought to combine with oxygen.

Mercury is oxidized by long continued agitation in a bottle half filled with atmospherical air, and is converted into a black powder to which Boerhaave gave the name of *ethiops per se*. In this the oxide is mixed, however, with much metallic mercury. The black oxide may be obtained with less trouble, by triturating calomel with an excess of a hot solution of potassa or soda,edulcorating with cold water, and drying at the temperature of the atmosphere in a dark place; or it may be obtained by precipitating carefully prepared proto-nitrate by lime-water. When this oxide is distilled in a glass retort, oxygen gas is evolved; or, if long heated with access of air, it acquires a reddish colour, and a still farther dose of oxygen.

The protoxide of mercury, it is asserted by Guibourt, cannot, however, be obtained perfectly pure; for when either pronitrate or protochloride of mercury is decomposed by potassa, the precipitate, even when excluded from air, contains peroxide of mercury and small globules of metal, the latter of which are discoverable by a magnifier. Nor can it be procured by triturating the peroxide with metallie mercury. (6 Ann. de Ch. et Ph. ii. 422.) This assertion, however, which he has extended to the protosulphuret, has been satisfactorily refuted, so far as respects the latter compound, in the Quarterly Journal, xviii. 291.

Another oxide of mercury is obtained by exposing the fluid metal for several days to nearly its boiling temperature, in a flat glass vessel, into which air is freely admitted. After a sufficient length of time, small flaky crystals form on its surface, of a brownish red, or flea colour. This red oxide was formerly called *precipitate per se*. When distilled alone in a glass retort, it yields remarkably pure oxygen gas, and returns to a metallic

state. It is composed, according to Fourcroy and Thenard, of 100 metal and 8 of oxygen. Sir H. Davy also found its oxygen to be exactly double that of the *protoxide*, which from his experiments is composed of 190 mercury, and 7.5 oxygen, while the peroxide consists of 190 metal and 15 oxygen. It will be sufficiently near the truth, if we admit, with Dr. Wollaston, that, according to the original determination of Fourcroy and Thenard, confirmed by the recent experiments of Sefstrom, the black oxide consists of 100 metal, united with 4 of oxygen, and the red of 100 mercury + 8 oxygen. (Ann. of Phil. N.S. ii. 126). The latter number agrees also with the experiments of Guibourt; and the oxygen in the protoxide, though, from his analysis, it appeared to amount to  $4\frac{1}{2}$  oxygen upon 100 mercury, may be safely taken at half that in the peroxide. We may consider, then, the two oxides of mercury to be composed as follows:

	Mercury.	Oxygen.	Merc.	Oxyg.	At. wt.
Protoxide ..	100	.... 4	.... 1 atom	+ 1 atom	.. 208
Peroxide ..	100	.... 8	.... 1 atom	+ 2 atoms	.. 216

Peroxide of mercury, Guibourt finds, is decomposed by long continued exposure to light. It is sparingly soluble in water, and communicates to it the property of turning syrup of violets green, and of being precipitated by sulphureted hydrogen. With ammonia, the peroxide forms an *ammoniuret of mercury*, decomposable by heat.

*Chlorides of mercury.*—Mercury unites easily with chlorine, and, if heated in that gas, burns with a pale red flame. The product is identical with the salt called *corrosive sublimate*, which, in fact, is a chloride of mercury, and is termed *perchloride* or *bi-chloride* to distinguish it from *calomel*, another compound of the same elements in different proportions. The bi-chloride is constituted of

Mercury	.... 74	.... 100.	.... 1 atom	200
Chlorine	.... 26	.... 35.2	.... 2 atoms	72
	<hr style="width: 50%; margin: 0 auto;"/>		Weight of its atom	<hr style="width: 50%; margin: 0 auto;"/>
	100			272

When the bi-chloride is accurately mixed with about half its weight of metallic quicksilver, and sublimed, we obtain a compound of chlorine and mercury, called *proto-chloride of mercury* or *calomel*, a substance long used, and of great importance in medicine. It is constituted of

Mercury . . . . 85	. . . . 100.	. . . . 1 atom	200
Chlorine . . . . 15	. . . . 17.6	. . . . 1 atom	36
100		Weight of its atom	236

Corrosive sublimate and calomel are not, however, prepared for use by the direct combination of chlorine and mercury, but by a method which will be described in speaking of the sulphate.

*Bi-chloride of mercury* is a white semi-transparent mass, sometimes perfectly crystallized. (An. of Phil. N. S. vi. 285.) Its specific gravity is 5.2. Light has no action on it in its solid form. It has an acrid and nauseous taste, and leaves in the mouth a permanent metallic flavour. It is a violent poison. Water at 60° Fahr. dissolves rather more than one-twentieth of its weight. The liquid reddens litmus, but the colour is restored by the chlorides of potassium, sodium, lithium, barium, strontium, calcium, &c. (34 An. de Ch. et de Ph. 143.) The solution is decomposed by light, and calomel is formed. Alcohol, sp. gr. .816, takes up half its weight, and acquires the sp. gr. 1.08. Ether, sp. gr. .745, dissolves one-third of its weight, and the solution has the same specific gravity as that effected by alcohol. Camphor causes both these solvents to take up a much larger proportion of corrosive sublimate. Muriatic acid, sp. gr. 1.158, at 70° Fahr. takes up twice its weight of corrosive sublimate, and the solution is of sp. gr. 2.412; but, on lowering its temperature a few degrees, it suddenly becomes solid. From Dr. Davy's experiments (Phil. Trans. 1822), corrosive sublimate appears not to be soluble in the sulphuric or nitric acids. It is capable of uniting and forming a double salt, with muriates of ammonia, potassa, soda, baryta, and magnesia, all of which greatly increase its solubility; and the solutions by these menstrua, as well as by alcohol and ether, Dr. Davy finds, undergo no change by exposure to the light. When dissolved in water, it is to be presumed that each atom of bi-chloride decomposes 2 atoms of water, the oxygen of which forms 1 atom of deutoxide of mercury, while the hydrogen forms with the 2 atoms of chlorine an equivalent quantity of muriatic acid, which with the peroxide composes muriate of mercury. From the watery solution, alkalis throw down peroxide of mercury, first as an orange, and afterwards as a brick-red precipitate.

From its acid re-agency, as well as from its forming a distinct

class of salts with the chlorides of potassium, sodium, &c. Bonsdorff has been led to consider corrosive sublimate as an acid, to which he gives the name of *chloro-hydrargyric*; and to the salts, which it forms with bases, that of *chloro-hydrargyrates*. He extends the same nomenclature to the chlorides of other metals, as *chloro-platinates*, *chloro-palladiates*, *chloro-stannates*, &c. The compounds of iodine admit of a similar view. The deut-iodide of mercury, though insoluble in water, readily dissolves in solutions of the iodides of potassium, sodium, &c. and forms crystallizable compounds. (An. de Ch. et Ph. xxxiv. 142.) The facts, stated by Bonsdorff, are valuable, but the explanation, as Liebig has shown (xxxv. 68), does not embrace all the phenomena, which require further investigation.

*Proto-chloride of mercury (calomel)* is white, crystalline, and very heavy, its specific gravity being 7.2. It is tasteless, and nearly insoluble; and may be taken in doses of several grains, without any effect but that of a purgative. When a mass of it is scratched, it gives a yellow streak, which is not the case with the perchloride; and, when very finely powdered, it has a light buff colour. It is decomposed when boiled with a solution of muriate of soda, and still more readily and completely by muriate of ammonia, which converts it entirely into bi-chloride and mercury, the former remaining in solution. (Hennell, in Quart. Journ. xviii. 295.) If therefore either of these salts be employed, as is recommended, to dissolve any corrosive sublimate remaining in calomel, they should be used only in cold and very dilute solutions.

*Mercury and iodine.*—There are two compounds of these bodies, which may be formed either by gently heating mercury with iodine, or by mixing solutions of mercury with hydriodic acid. Both are insoluble. The prot-iodide, consisting of 1 atom of mercury + 1 of iodine, is yellow. The deut-iodide, consisting of 1 mercury + 2 iodine, has a fine red colour.

*Mercury and cyanogen.*—This compound may be prepared by boiling in a matras eight parts of water, two of finely powdered prussian blue, and one of peroxide of mercury. When the liquid assumes a yellow colour, it is to be filtered, and the bi-cyanide of mercury is deposited in regular crystals, described Ann. of Phil. N.S. vi. 42. Mr. Turner recommends that the prussian blue should be previously purified by digestion in dilute muriatic acid; and that of this, well washed and dried,

eight parts should be boiled with eleven of peroxide of mercury in a sufficient quantity of water. A colourless liquid is obtained, which yields pure white crystals of bi-cyanide of mercury even to the last drop. The same writer prefers, also, to use pure ferrocyanate of iron prepared from ferro-cyanate of potash and a persalt of iron. Of this, one part is equivalent to two of prussian blue. (Brewster's Journ. v. 245.) If intended for the preparation of cyanogen, the salt must be thoroughly dried; avoiding, however, more heat than is absolutely necessary.

### *Salts of Mercury.*

*Proto-sulphate.*—Mercury is dissolved by hot and concentrated *sulphuric acid*. Two parts of sulphuric acid and one of mercury are the proportions generally used; and, as strong sulphuric acid acts but little on iron, the combination on a large scale may be made in an iron vessel; but, for delicate purposes, one of glass should be used. The proto-sulphate is deposited in fine white scaly crystals, which, when washed with a little water, and dried on blotting paper, probably consist of 1 atom of acid, 1 of protoxide, and 2 atoms of water. When the sulphate is heated for some time, at a temperature exceeding that of boiling water, it loses still more acid, and is changed into a hard grey mass. When this is removed from the fire, and boiling water poured upon it, a lemon-yellow coloured powder is formed, called *Turbith mineral*. This substance requires for solution 2000 times its weight of water.

The principal use of sulphate of mercury is in the formation of corrosive sublimate and calomel. The following methods of preparing these compounds have been described by Mr. Brande: For corrosive sublimate, 50 pounds of mercury are boiled to dryness in a cast-iron pan with 70 pounds of sulphuric acid; 73 pounds of super-sulphate of mercury are thus formed, which being perfectly mixed with 120 lbs. of muriate of soda and sublimed, yield from 63 to 65 lbs. of corrosive sublimate.

To form calomel, 50 lbs. of mercury are boiled with 70 lbs. of sulphuric acid to dryness: 62 lbs. of the dry salt are triturated with  $40\frac{1}{2}$  lbs. of mercury until the globules disappear, and 34 lbs. of common salt are then added. The mixture is submitted to heat in earthen vessels, and from 95 to 100 lbs. of calomel are the result. This is first to be ground to a fine and

impalpable powder, and then washed with large quantities of distilled water. (Manual, vol. ii.)

*Chlorates of mercury.*—The oxides of mercury dissolve in chloric acid. The salt formed with the peroxide is the most soluble. When heated, both give out oxygen gas, and are converted into peroxide of mercury and corrosive sublimate. (Vauquelin, Ann. de Chim. xcv. 103.)

*Proto-nitrate of mercury.*—Nitric acid dissolves mercury, both with and without the assistance of heat. Mr. Dalton advises 500 grains of mercury to be put to 1000 water grain measures of acid, sp. gr. 1.2. At the common temperature, but little nitrous gas is evolved; and the acid becomes slowly saturated. The solution is very ponderous and colourless; and does not become milky when mingled with water. Pure fixed alkalis give a yellowish white precipitate; and ammonia a greyish black one.

A nitrate of mercury, in which the oxide is at the minimum, may also be prepared by using a stronger acid, provided the metal is in excess. On crystallizing the solution, Mitscherlich has observed, that the salt which is obtained, though always a protonitrate, varies as to the proportion of acid and base. To obtain a neutral compound, the solution must contain a considerable excess of free acid, for otherwise the acid only suffices to oxidize the mercury, and the neutral compound, which is at first formed, takes up a farther proportion of oxide, and forms a salt with excess of base. By acting upon either of these salts with water, hot or cold, variously coloured precipitates are obtained, which are not to be considered as definite compounds, but as mixtures of various subsalts, with or without oxide of mercury.

The neutral proto-nitrate of mercury consists, according to Mitscherlich's analysis, of 1 atom of nitric acid, 1 of oxide, and 2 of water; the sub-proto-nitrate, obtained from the same solution with mercury in excess, of 2 atoms of acid, 3 atoms of protoxide, and 3 of water. (35 Ann. de Ch. et de Ph. 421.)

*Pernitrate.*—When heat is used in dissolving mercury in nitric acid, and a greater proportional quantity of acid is employed, (for instance, 1000 water gr. measures, of density 1.2, to 350 grains of mercury) a brisk effervescence arises, occasioned by the escape of nitrous gas, and a solution is

obtained, in which the metal is oxidated to the maximum, constituting *per-nitrate of mercury*. When this solution is allowed to cool, it forms transparent and colourless rhombic prisms, constituted of 1 atom of acid, 2 atoms of peroxide, and 2 atoms of water. But, if poured into cold water, a yellowish white sediment is formed; or, if into boiling water, an orange-coloured one. Both precipitates consist of nitric acid, with a great excess of oxide, forming an insoluble *sub-pernitrate of mercury*; and, by very copious washing, the peroxide itself may be obtained.

If a solution of the pernitrate be boiled with a fresh quantity of mercury, the newly added metal is taken up, without any discharge of nitrous gas, the metal becoming oxidized at the expence of that already dissolved.

When the nitrate of mercury is exposed to a heat gradually raised to 600° or upwards, it is deprived of water and of most of its acid, and reduced to an oxide, which has the form of brilliant red scales. This substance, commonly called *red precipitate*, is termed more properly the *nitrovide of mercury*; because it still contains a small proportion of acid, which is decomposed by heat, and deteriorates the oxygen gas obtained by its distillation.

*Nitrates of mercury and ammonia.*—Both the protoxide and peroxide of mercury are capable of forming double salts with ammonia and nitric acid. The first is equivalent to 1 atom of nitrate of ammonia and 3 of protoxide; the second to 2 atoms of nitrate of ammonia and 3 of peroxide. (Mitscherlich.)

*White precipitated mercury.*—The substance used in medicine under this name has been shown by Mr. Hennell to consist of

1 atom of peroxide of mercury . . . . .	216
1 atom of muriate of ammonia . . . . .	54
	270

Beside this, there is also a soluble ammonia-muriate (*sel alembroth*) formed by dissolving equal weights of bi-chloride of mercury and muriate of ammonia in water, and crystallizing. This salt has been analyzed by Soubeiran. (Ann. de Ch. et de Ph. vol. 34, 35.)

*Fulminating mercury.*—Mercury is the basis of a *fulmi-*

*nating compound* discovered by the late Mr. E. Howard. To prepare this powder, 100 grains (or a greater proportional quantity, not exceeding 500) are to be dissolved, with heat, in a measured ounce and half of nitric acid. The solution being poured cold upon two measured ounces of alcohol, previously introduced into any convenient glass vessel, a moderate heat is to be applied till effervescence is excited. A white fume then begins to undulate on the surface of the liquor, and the powder will be gradually precipitated on the cessation of action and re-action. The precipitate is to be immediately collected on a filter, well washed with distilled water, and cautiously dried in a heat not exceeding that of a water-bath. The immediate washing of the powder is material, because it is liable to the re-action of the nitric acid; and, while any of that acid adheres to it, it is very subject to be decomposed by the action of light. From 100 grains of mercury, about 120 or 130 of the powder are obtained. (Phil. Trans. 1800, page 214.) This powder has the property of detonating loudly in a gentle heat, or by slight friction. Hence it has been proposed as a means of firing ordnance. But an accident described by Professor Silliman, as having happened in his laboratory, shows that this fulminating compound explodes from such trifling causes, as not to be kept without danger, even when secured from friction or heat. (Edinb. Phil. Journ. i. 417.) It has been shown by the experiments of Liebig and Gay Lussac, (Ann. de Ch. et de Ph. xxiv. and xxv.) that fulminating mercury owes its properties to a peculiar acid, united with oxide of mercury, which may be transferred from it to alkaline and other bases, but is not obtainable in a separate state. Of this acid, to which they have given the name of the *fulminic*, more will be said in treating of fulminating silver.

*Sulphurets of mercury.*—By combination with sulphur, mercury affords two distinct compounds. By long continued trituration, these two bodies unite, and form a black sulphuret, called formerly *ethiops mineral*, which is not soluble without decomposition in alkaline solutions, but dissolves readily in nitric acid. When united together by fusion, and afterwards sublimed, they constitute a red sulphuret called *cinnabar*, which, when powdered, affords the common pigment vermilion. The process used by the Dutch, who have long been celebrated for the preparation of cinnabar, is described in the 4th volume



of the *Annales de Chimie*, or in Aikin's Dictionary, vol. ii. This compound also may be obtained by mixing concentrated solutions of muriate of mercury and hydro-sulphuret of ammonia. A brownish muddy precipitate is obtained, which, when left undisturbed, turns yellow in three or four days, then orange, and finally acquires a beautiful cinnabar colour. (Nicholson's Journal, 8vo. i. 299.) It is from a natural compound of mercury and sulphur, called *native cinnabar*, that most of the mercury of commerce is obtained, by distilling the compound with iron filings. It may, also, according to Berthier, be advantageously separated, by substituting for iron a mixture of charcoal and quicklime.

The composition of the sulphurets of mercury has been investigated experimentally by Guibourt. (Ann. de Ch. et de Ph. ii. 425.) The first he obtained by acting with sulphureted hydrogen on calomel; and the second on corrosive sublimate. Both the resulting compounds are black; but the latter is entirely convertible into cinnabar of the usual colour by sublimation, while the former is resolved by heat into quicksilver and bi-sulphuret. Analysis, by distillation with iron, showed them to consist as follows:

	Atoms of		Atomic
	Mercury.	Sulphur.	Weight.
Proto-sulphuret . . . .	100	8.2	1 + 1 .. = 216
Bi-sulphuret . . . . .	100	16.0	1 + 2 .. = 232

Sulphuret of mercury has been shown by Mr. H. Rose to form compounds in atomic proportions with chloride, iodide, bromide, and fluoride of that metal. The chloro-sulphuret of mercury is obtained by transmitting a current of sulphureted hydrogen through a solution of bi-chloride of mercury. The precipitate is at first white, and remains in suspension in the liquid, but, after standing, it may be separated by the filter. It consists of 1 atom chloride of mercury + 2 atoms of the sulphuret of that metal. The nitrate of peroxide of mercury also forms a definite compound with sulphuret of mercury. (Ann. de Ch. et de Ph. xl. 46.)

*Amalgams.*—Mercury dissolves gold, silver, tin, and many other metals; and, if these be combined with it in sufficient quantity, the mercury loses its fluidity, and forms an amalgam. A solid amalgam of lead, and another of bismuth, on admixture together, have the singular property of instantly becoming fluid.

The extraordinary powers of the base of ammonia in amalgamating with mercury, have already been described in speaking of that alkali.

By combination with mercury, metals that are not easily oxidized acquire a facility of entering into union with oxygen. Thus gold and silver, when combined with mercury, are oxidized by agitation in contact with air. This fact furnishes a striking illustration of the effect of overcoming the aggregative affinity of bodies in promoting chemical union.

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## SECTION XXXIV.

### *Silver.*

Silver is a metal which admits of a degree of lustre inferior only to that of polished steel. Its specific gravity, after being hammered, is 10.51. In malleability, ductility, and tenacity, it exceeds all the metals except gold. Its fusing point, as determined by Dr. Kennedy, is  $22^{\circ}$  of Wedgwood's pyrometer. By considerably raising the heat, it may be volatilized; and by slow cooling of the fused mass, it may be made to assume a regular crystallized form.

To obtain silver in a state of purity, Mr. Donovan recommends that 240 grains of standard silver be dissolved in as much pure nitric acid, of specific gravity about 1.2, as will be barely necessary for solution. This is to be filtered, and distilled water allowed to run through the filter, until the fluids amount to two ounce measures. A bright plate of copper, weighing upwards of 64 grains, is to be immersed and frequently agitated in it. When the silver has entirely precipitated, which will very soon happen, the clear supernatant liquid is to be poured off, and the precipitate to be well washed with pure water. The silver is next to be boiled for a few minutes in liquid ammonia. It is then to be well washed with water, and dried on a filter; after which, if required, it may be melted in a crucible. (Phil. Mag. xlvii. 205.) Dr. Thomson found it difficult to obtain silver free from copper, even when reduced from the chloride, but accomplished the object by first washing the chloride with diluted nitric acid, which removed the copper. (First Princ. ii. 436.)

The chemical properties of silver are the following :

*Oxides of silver.*—Silver is difficultly oxidized by the concurrence of heat and air. The *tarnishing* of silver is owing not to its oxidation merely, but to its union with sulphur, as Proust has satisfactorily shown.

By transmitting a Galvanic or electric discharge through silver wire, it is oxidized ; and by long exposure of silver to heat, with free access of air, it is at length converted into an olive-coloured glass.

From some curious facts, which are stated by Mr. Lucas in vol. iii. N. S. of the Manchester Society's Memoirs, it appears that silver, when melted, and exposed to a current of air or of oxygen gas, forms a temporary union with oxygen, which is again given off in the state of gas, when the metal cools spontaneously, or is poured into cold water. This property, it has been shown by Chevillot, (Ann. de Ch. et de Phys. xiii. 299,) belongs only to pure silver, and not to silver alloyed even with a very small proportion of copper.

The oxide of silver may be obtained by decomposing nitrate of silver with solution of baryta ; and, after washing the precipitate sufficiently, heating it to dull redness. It has an olive colour, and is composed, according to Sir H. Davy, of 100 parts of silver united with 7.3 oxygen, or, according to Dr. Wollaston's scale, 7.4. A larger proportion of oxygen was formerly assigned by Berzelius ; but he has given the following statement (Ann. of Phil. xv. 93) :

Silver . . . . .	93.12	....	100.
Oxygen . . . . .	6.88	....	7.3986
	100.		107.3986

Taking the proportion of oxygen which combines with 100 parts of silver at 7.3, the equivalent number for silver will be 110. No other oxide of silver has been actually ascertained to exist ; though, from the experiments of Mr. Faraday, there seems reason to believe that the pellicle, which forms spontaneously on an ammoniacal solution of oxide of silver exposed to the air, is a protoxide of that metal, in which the oxygen is to the silver as 7.5 to 157.4. (Journ. of Science, iv. 270.) Dr. Thomson admits it to be a distinct oxide, and considers it as constituted of 3 atoms of silver = 330 + 2 atoms of oxygen

= 16. It does not appear, however, to form distinct salts with acids.

*Chloride of silver.*—Silver combines with chlorine, under some circumstances, with the appearance of combustion. The result is a substance called *chloride of silver*, which may be obtained more easily by adding a solution of nitrate of silver to one of chloride of sodium (common salt) andedulcorating and drying the precipitate. This precipitate, if exposed to the light, and especially to the sun's direct rays, becomes darker in colour, and finally black. When heated to dull redness in a silver crucible, it melts, and on cooling forms a mass, which has the imperfect transparency of horn, and has hence been called *luna cornea*, or *horn silver*. It was formerly considered as a compound of oxide of silver with dry muriatic acid, and its composition was stated as follows. One hundred grains contain,

	Acid.	Base.
According to Dr. Marcet . . . .	19.05	. . . . 80.95
————— Gay Lussac . . . .	19.28	. . . . 80.72
————— Berzelius . . . . .	19.035	. . . . 80.965

Horn silver is now more properly regarded as a chloride of that metal. To convert the old statement of its composition into the new, it is only necessary to calculate the oxygen contained in the oxide, to add it to the muriatic acid, and to consider the sum as chlorine. To determine experimentally the composition of chloride of silver, 100 grains of the metal may be dissolved in nitric acid, and precipitated by a solution of common salt. The precipitate being carefully washed with water slightly acidulated with nitric acid, dried, and fused, the increase of weight on the silver shows the quantity of chlorine which has been gained. Different chemists have given different statements. Wenzel found that 100 of silver gave 131.4 of fused chloride; Davy, 132.5; Bucholz, Rose, Marcet, and Gay Lussac, 133.3; and Berzelius, from several experiments, considers 132.75 as the true product. (Ann. of Phil. xv. 93.) Taking Sir H. Davy's result, the composition of the chloride of silver is

Silver . . . . .	75.5	. . . . 100.	. . . . 307.69
Chlorine . . . .	24.5	. . . . 32.5	. . . . 100.

100.

And the equivalent number for silver, deducible from this analysis, is 110.7, from Berzelius's 109.9. It will perhaps be

very near the truth if taken at 110, a number agreeing with that indicated by the composition of the oxide, and confirmed by experiments made with great care by Dr. Thomson on the synthesis of the chloride.

Chloride of silver is insoluble in water, but is very soluble in liquid ammonia. The solution sometimes, when heated, affords fulminating silver, and should therefore be treated with caution. It furnishes crystals, which, by exposure to the air, are decomposed, the ammonia escaping, and chloride of silver remaining. Chloride of silver also dissolves in hypo-sulphurous acid. It is decomposed by a stream of hydrogen gas, and, when moistened with water, by any materials capable of affording hydrogen, such as zinc filings and dilute sulphuric acid. Zinc and tin decompose it also in the dry way.

If a little fused chloride of silver and a little zinc be heated together in a glass tube, a violent action takes place, chloride of zinc is formed, and silver set at liberty, and the heat generally rises high enough to fuse the silver. Zinc alone, brought into contact with moist chloride of silver, decomposes it; but hydrogen, freed from all impurities, and directed upon moistened chloride of silver in the dark, effects no change whatever. (Faraday, Journ. of Science, viii. 375.)

*Iodide of silver* is formed, when hydriodic acid is added to nitrate of silver. It is insoluble both in water and ammonia; has a greenish yellow colour; and is decomposed when heated with potassa. It consists of a single atom of each element.

*Cyanide of silver* is precipitated in a white curdy form from the nitrate, by hydro-cyanic acid, or an alkaline hydro-cyanate. It is insoluble in nitric acid and in water, but dissolves in liquid ammonia.

#### *Salts of Silver.*

*Chlorate of silver* may be obtained by digesting oxide of silver with chloric acid. It forms small rhomboidal crystals.

*Iodate of silver* is precipitated by iodic acid from the nitrate. It is a white powder, insoluble in water, but very soluble in ammonia.

*Hypo-sulphite of silver* may be formed by mixing hypo-sulphite of soda with dilute nitrate of silver, or by dissolving chloride of silver in any of the hypo-sulphites. Though formed of ingredients that have a metallic and very bitter taste, its flavour is intensely sweet.

*Sulphate of silver.*—Sulphuric acid acts on silver when heated, oxidizes and dissolves it; but the sulphate of silver, which is a very useful test, is better formed by precipitating nitrate of silver with carbonate of soda,edulcorating the precipitate, and dissolving it in dilute sulphuric acid. It forms small brilliant needle-shaped crystals, which require about 90 parts of water at 60° for solution, but dissolve more readily in hot water. It is anhydrous, and is constituted of 1 atom of acid and 1 atom of base.

*Nitrate of silver.*—Nitric acid, diluted with from two to four parts of water, dissolves silver with a disengagement of nitrous gas. If the silver be pure, the solution is colourless, otherwise it has a green hue. According to Proust, nitrate of silver already saturated, if boiled with powdered silver, dissolves an additional quantity; and a solution is obtained, in which the silver is oxidized at a minimum. (Nicholson's Journ. xv. 376.)

Nitrate of silver forms by spontaneous evaporation large and regular crystals, which are flat rhombs, soluble in about an equal weight of water, and in four parts of alcohol. It is anhydrous, and consists of

Nitric acid	.....	32.92	or 1 atom	54
Oxide of silver	.....	67.08	or 1 atom	118
<hr style="width: 20%; margin: 0 auto;"/>				
100.				<hr style="width: 20%; margin: 0 auto;"/> 172

Nitrate of silver is decomposed by muriatic acid, the hydrogen of that acid passing to the oxygen of the oxide, and the chlorine uniting with the silver. Chlorine, also, decomposes nitrate of silver, as do the solutions of chlorides and muriates in water. (Ann. of Phil. N. S. iii. 314.) By this property, silver may be separated from several other metals. When standard silver, for instance, is dissolved in nitric acid, and a solution of common salt is added to the liquid, an insoluble chloride of silver falls down, and the copper remains in solution. From the chloride of silver, the pure metal may be obtained, by drying it and fusing it with twice its weight of potassa or soda. (See Ann. of Phil. xv. 389.)

A solution of nitrate of silver stains animal substances a deep black. Hence it has been used for the staining of hair; but, when thus employed, it should be very much diluted, and used with extreme caution, on account of its corrosive quality.

White paper, or white leather, when stained with a solution

of nitrate of silver, in the proportion of ten parts of water to one of the salt, undergoes no change in the dark; but when exposed to the light of day, it gradually acquires colour, and passes through a succession of changes to black. The common sunbeams, passing through red glass, have very little effect upon it; yellow and green are more efficacious; but blue and violet produce the most decidedly powerful effects. Hence this property furnishes a method of copying paintings on glass, and transferring them to leather or paper. The process is described by Mr. T. Wedgwood, in Nicholson's Journal, 8vo. iii. 167.

By a similar process, ivory may be covered with silver. Let a slip of ivory be immersed in a dilute solution of pure nitrate of silver, till the ivory has acquired a bright yellow colour. Then remove it into a tumbler filled with distilled water, and expose it to the direct light of the sun. After two or three hours' exposure, it will have become black; but on rubbing it a little, the surface will be changed into a bright metallic one, resembling a slip of pure silver. As the solution penetrates deep into the ivory, the bright surface, when worn away, is replaced by a succession of others.

Crystals of nitrate of silver fuse when heated; and being poured, in this state, into heated moulds, form the common *lunar caustic*. The indelible ink, used for marking linen and cotton with a pen, may be prepared by dissolving 2 drachms of lunar caustic, the purity of which is for this purpose important, and 1 drachm of gum arabic, in 7 drachms of distilled water, colouring the liquid with a little China ink. The preparatory liquid for moistening the cloth is made by dissolving 2 ounces sub-carbonate of soda and 2 drachms of gum arabic in 4 ounces of water. (Quart. Journ. xxii. 407.)

Nitrate of silver is decomposed by other metals. Thus the surface of a plate of copper, to which the solution is applied, becomes plated over with silver. The latter portions contain an admixture of copper, which may be removed by a fresh solution of nitrate of silver. If a little mercury be poured into a bottle filled with the solution of nitrate of silver, and the bottle be left some time undisturbed, the silver is precipitated of a beautiful form resembling the branches of a tree, which has been termed *Arbor Dianæ*. The most successful process for obtaining this appearance, Baumé finds to be the following: Mix together six parts of a solution of silver in nitric acid, and

four of a solution of mercury in the same acid, both completely saturated. Add a small quantity of distilled water; and put the mixture into a conical glass vessel, containing 6 parts of an amalgam, made with 7 parts of mercury and 1 of silver. At the end of some hours, there appears on the surface of the amalgam a precipitate in the form of a vegetation. According to Proust, however, this complicated process is quite unnecessary; and all that is required is to throw mercury into nitrate of silver very much diluted. A beautiful arborization of reduced silver, he observes, will be produced without difficulty.

The solution of nitrate of silver is decomposed by charcoal, and by hydrogen gas and its compounds. This may be shown by experiments precisely similar to those already directed to be made with muriate of gold. A stick of clean phosphorus, also, immersed in a dilute solution of nitrate of silver, in the course of a few days becomes beautifully gilt.

*Muriatic acid* does not act on metallic silver, except by long continued boiling, and then only in a small degree. But when two small slips of zinc and of silver are fastened together, and immersed in dilute muriatic acid, the silver, being rendered negative by the zinc, acquires a coating of chloride of silver.

A very useful solvent of silver has been discovered by Mr. Keir of Birmingham. It is formed by dissolving one part of nitre in about eight or ten parts by weight of concentrated sulphuric acid. This compound (which may be called *nitro-sulphuric acid*), when heated to between  $100^{\circ}$  and  $200^{\circ}$  Fahr., dissolves one-fifth or one-sixth its weight of silver, with an extrication of nitrous gas; and leaves, untouched, any copper, gold, lead, or iron, with which the silver may be combined. Hence it is a most useful agent in extracting silver from old plated goods. The silver may be recovered from the solution by adding muriate of soda, which forms chloride of silver; and this may be decomposed by carbonate of soda, in the way which has already been described.

*Phosphate of silver* is a compound of some importance, from its use in preparing chloric acid. To obtain it, crystals of nitrate of silver may be dissolved in pure water, and a solution of phosphate of soda be added. The neutrality of the nitrate of silver is destroyed, and though the phosphate contains an excess of alkali, the resulting liquor is acid. The precipitate is of a yellow colour. When washed and dried, it is fusible at



a red heat without any farther loss of weight. It consists, according to Berzelius, of

Phosphoric acid . . . . .	17.025	. . . . .	100.
Oxide of silver . . . . .	82.975	. . . . .	487.38
	<hr/>		
	100.		

Hydro-cyanic acid and hydro-cyanate of potassa decompose the solutions of silver, and precipitate a cyanide of that metal, from which cyanogen may be separated by heat. The ferro-prussiates throw down a precipitate which is at first white, but by exposure to the light becomes blue.

*Chromate of silver* has been obtained, in crystals sufficiently distinct to admit of the admeasurement of their angles, by allowing a solution of chromate of potassa, after separating the precipitate occasioned by nitrate of silver, to evaporate spontaneously. They are of a deep red colour, have a strong metallic lustre, and are insoluble either in cold or hot water. (Phil Mag. May 1827. p. 345.)

*Processes for preparing fulminating silver.*—Precipitate nitrate of silver by lime-water, and thoroughlyedulcorate and dry the precipitate. Let this be afterward put into a vessel of the purest liquid ammonia, in which it may remain for ten or twelve hours. It will then assume the form of a black powder, from which the fluid is to be decanted, and the black substance left to dry in the air. Or dissolve chloride of silver in liquid ammonia, and add fragments of caustic potassa. An effervescence will take place; when this has ceased, dilute and filter the black liquid which results. There remains, on the filter, a black powder, which must be carefully dried at the temperature of the atmosphere. (Quart. Journ. July 1808.) This is the celebrated compound termed *fulminating silver*, which detonates with the gentlest heat, and even with the slightest friction. It may be formed, also, by boiling any precipitated oxide of silver, for a few moments, in a mixed solution of potassa and ammonia. The protoxide, however, described by Mr. Faraday, does not afford it. When once prepared, no attempt must be made to enclose it in a bottle, and it must be left undisturbed in the vessel in which it was dried. Great caution is necessary in the preparation of this substance, for in making experiments on it, several fatal accidents have been produced by indiscretion in its use. It

even explodes, when moist, on the gentlest friction. (See Count Rumford's papers, Phil. Trans. 1798.)

Another detonating compound of silver, formed by a process similar to that employed in making the fulminating mercury of Mr. Howard, has been described by Descotils. (Nicholson's Journal, xviii. 140.) It is prepared by adding alcohol to a heated solution of silver in nitric acid, while the solution is yet going on. Considerable effervescence arises; the liquor presently becomes turbid; and a heavy, white, crystalline powder falls down. This, when washed and dried, is the *detonating silver*. Heat, a slight blow, or long-continued friction, causes it to inflame with a brisk detonation. Pressure alone is not sufficient unless very powerful. It detonates by the electric spark, and is set on fire with an explosion by concentrated sulphuric acid. Both in the preparation of this substance, and in experiments on its detonation, much caution is necessary; and only very small quantities should be employed. In repeating the process, Mr. Cruickshank dissolved 40 grains of silver in 2 ounces of strong nitric acid, diluted with an equal weight of water. Then by heating the solution with 2 ounces of alcohol, he obtained 60 grains of a white powder, which detonated violently. Liebig prepares it by dissolving a drachm of refined silver in half an ounce of nitric acid sp. gr. 1.52; 2 ounces of alcohol sp. gr. 0.85 are then added, and the whole is gradually raised to ebullition in a matrass. White crystalline flocculi soon appear, and it is then time to discontinue the application of heat. The ebullition, however, continues, and the precipitate increases in quantity. At this time it is important to prevent too rapid cooling, which diminishes the quantity of the product. The proportions of acid and alcohol, also, which have been recommended, are found to answer better than any others. Fulminating silver, thus prepared, has the form of white silky crystals; it detonates by the smallest shock even under water, by an increase of temperature, or the contact of sulphuric acid; it dissolves completely in 36 times its weight of boiling water, and separates again on cooling.

*Fulminic acid*.—Fulminating silver, it has been shown by Liebig, contains a peculiar acid, the *fulminic*, which is separated by all alkaline and earthy bases except ammonia, 31.25 per cent. of oxide of silver remaining. All these new compounds are crystallizable, and detonate strongly. A portion of

silver seems to accompany the acid into these combinations, for copper precipitates silver from fulminate of potassa. Indeed a metallic base appears to be necessary to the permanent existence of this acid, whose constituent principles without such a base, or rather element, appear to be held together by a very feeble attraction. This metallic ingredient differs with the source from which the fulminating compound has been prepared, and it may be either silver, mercury, copper, zinc, or iron.

By decomposing fulminating silver with peroxide of copper, carbonic acid and nitrogen gases are obtained, in the same proportions as from the combustion of cyanogen. Of oxide of silver it appears to contain two portions, the one serving as an element of the acid, the other as a base. In 100 parts of the fulminating silver, 38 of oxide fulfil the former function, and 38 the latter. The *fulminates* all contain a common principle of fulmination independently of their bases; and this common ingredient consists of 1 atom of cyanogen and 1 atom of oxygen, forming *cyanic acid*, which, with a metallic element, differing in the several fulminates, constitutes *fulminic acid*. The best way of transferring the fulminic acid from oxide of silver to potassa, is to act upon fulminating silver with chloride of potassium. Muriatic acid and hydriodic acid decompose fulminating silver with a disengagement of hydro-cyanic acid, and the formation of a new acid, constituted of chlorine (or iodine), carbon, and azote; which, when united with a base, reddens the persalts of iron. Sulphureted hydrogen, also, passed through a solution of fulminate of silver, causes the production of a new acid, which has the property of changing the colour of perchloride of iron to a deep red, without being first combined with a base. This acid contains sulphur, but yet differs from the sulphocyanic. At the same time, Liebig supposes that the cyanic acid of the fulminate is changed into cyanite of ammonia; but the precise nature of the changes that ensue requires to be more minutely investigated. (Ann. de Ch. et de Ph. xxxii. 316.)

*Sulphuret of silver.*—Silver is acted on by sulphurets of alkalis, and by sulphureted hydrogen gas. Both these substances blacken silver when exposed to their operation; and the common tarnishing of silver by the atmosphere has been traced to a similar cause. They precipitate silver, also, from all its solutions, of a black colour. Sulphuret of silver may also be formed by exposing sulphur and silver, stratified in a covered

crucible, to heat, till the excess of sulphur has been driven off. It has been analyzed by Berzelius, and found to consist of

Silver	87.032	.....	100.
Sulphur	12.968	.....	14.9
	100.		114.9

*Alloys.*—Silver is capable of being united with most other metals. When alloyed with copper, in the proportion of 0.90 to 11.10, it constitutes the *standard silver* of this country. This combination, though its colour differs but little from that of pure silver, is much harder, and better adapted for the purpose of coin, and of domestic implements. Silver of commerce is composed of 37 parts of fine silver to 3 of copper; but the fine silver, being obtained by cupellation, contains some gold, which is left after solution by acids, either in the form of purple protoxide, or black peroxide.

The object of *cupellation* is to oxidize the baser metals that may be mixed with silver; and to remove the oxide when formed, leaving the silver pure. To assist this, a proportion of some metal is added, which is not only readily oxidizable, but which affords a fusible oxide. Lead is generally employed for this purpose. A small shallow crucible, called a *cupel* (which is best made of the internal slough of a bullock's horn calcined to whiteness), is heated to redness under a muffle. Upon this a small button of pure lead is first placed; and then the silver, laminated, accurately weighed, and wrapped in lead-foil. The metals melt together, and an appearance called *fulguration*, or *scintillation*, ensues. The lead is gradually oxidized, and the oxide carries down the baser metals into the cupel, a button of pure silver being finally left. The process requires a nice regulation of the heat, and its success depends greatly on the skill and experience of the operator. In cooling the button, care also is necessary, as the accuracy of the result is apt to be destroyed by the spiriting of the fluid metal from beneath the congealed crust.

An ingenious application has lately been made, by Professor Oersted, of the electro-chemical properties of metals, acted upon by solvents, to the art of assaying silver. In many cases, the electricity evolved is so minute in quantity, as only to be appreciable by its effect on the magnetic needle. The more noble a metal, the greater the difficulty of its oxidation; and this

greater or less difficulty causes the needle to move more or less. It is easy then, by their comparative effects on the needle, to compare the oxidability of any two metals. Pure silver is more noble than its alloys, and its electro-magnetic effect being taken as a standard, the increase of alloy will be attended with an increased facility of oxidation. The effect, then, of silver, united with known progressive doses of alloy, may be made the basis of a scale, with which we may compare the effects of unknown alloys on the needle, and thus approach very nearly to their composition. As an art, however, this mode of assaying is yet in its infancy. (See Ann. de Ch. et de Ph. Nov. 1828.)

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## SECTION XXXV.

### *Gold.*

To obtain gold in a state of purity, one part by weight of standard gold may be dissolved in three of nitro-muriatic acid (composed, as Vauquelin recommends, of 1 part by weight nitric, and 2 muriatic acids); and to expel the excess of acid, the solution may be evaporated to dryness, taking care to use a gentle heat at the last. Redissolve the dry mass in water, and to the clear liquid add a solution of proto-sulphate of iron, as free as possible from per-sulphate, and a little exceeding four times the weight of the gold. The gold will be precipitated, perfectly metallized, in a fine powder, which, after being washed first with diluted nitric acid, and then with distilled water, may be either preserved for solution in powder, or fused into a mass.

The external qualities of gold are the following:

It has an orange or reddish yellow colour; and may be made to assume a degree of lustre inferior only to that of steel, platinum, silver, or mercury.

Its specific gravity varies a little according to the mechanical processes which it has undergone; but it may be stated, on the average, at 19.3.

It exceeds all other metals in ductility and malleability, and may be beaten into leaves  $\frac{1}{80000}$ th of an inch in thickness.

It is considerably tenacious; for a wire only  $\frac{7.8}{1000}$ ths of an inch diameter will sustain a weight of 150 lb.

Gold may be melted by a moderate red-heat, *viz.*, at about

32° of Wedgwood's pyrometer. The intense heat of a glass-house furnace has no other effect than to keep it in fusion. And even exposure to Mr. Parker's powerful burning lens, for several hours, occasioned no loss of weight. After fusion, it crystallizes in short quadrilateral pyramids.

Pure gold is not oxidized by exposure to heat with the access of air for any length of time; but it may be brought to the state of a purple powder, which, is probably an oxide, by transmitting through gold leaf or wire, either a powerful electrical or galvanic discharge. Macquer and Proust, however, conceive that this powder is nothing but gold reduced to an extremely fine state of division.

*Action of solvents.*—Sulphuric, nitric, and muriatic acids, have separately no evident action on gold; but the last-mentioned acid, Proust has observed, by long boiling with finely divided gold, dissolves a small portion. Neither does any acid, of which oxygen is the acidifying principle, except concentrated sulphuric and nitric acids, dissolve the oxides of gold, and even those acids do not form permanent compounds. Nitric acid, dissolves it only when heated, and deposits it again in the state of a hydroxide on adding water. Sulphuric acid, on the other hand, dissolves oxide of gold at common temperatures, but decomposes the oxide when heated in contact with it. (Pelletier, *Ann. de Ch. et de Phys.* xv.)

*Chlorides.*—The proper solvents of gold are chlorine and nitro-muriatic acid; and the latter, as Davy has shown, acts merely by the chlorine which it yields to the metal. Oberkampf prefers the former solvent, because a purer solution is obtained, and one which can more easily be freed from an excess of acid. (80 *Ann. de Chim.* 140.) Gold leaf, introduced into chlorine gas, takes fire and burns. But if gold leaf be suspended in water, into which chlorine gas is passed, it is quickly dissolved without effervescence. During its solution in nitro-muriatic acid, nitrous gas is evolved.

The solution of gold (in whatever way prepared) has an orange-yellow colour; but this, Oberkampf finds, is owing to an excess of acid, and it passes to a brownish red, as soon as the redundant acid is neutralized or expelled by heat. The solution should, therefore, be evaporated to dryness, and the dry mass (care being taken not to heat it too strongly) redissolved in water. Or, to avoid all risk of decomposition, the liquid may be removed from

the fire, when sufficiently concentrated to become solid on cooling. The solid obtained has a deep brownish red colour, is very fusible, and readily dissolves in water, giving a reddish yellow solution. The solution, Pelletier believes to be a real *chloride*, and not a *muriate*, though occasionally it contains a little free muriatic acid. If, instead of removing the mass from the fire, it be heated still longer, chlorine is disengaged, and a lemon-yellow compound is left, which he considers as a *sub-chloride*. By strongly urging the heat, the whole chlorine is expelled, and metallic gold only remains.

Concentrated sulphuric acid poured into the solution of gold, throws down an *anhydrous chloride*. If heat be applied, chlorine is disengaged, and a yellow sub-chloride falls; but if the heat be continued, metallic gold is separated. Arsenic and phosphoric acids produce the same effects.

According to Pelletier, there are two chlorides of gold.

	Metal.	Chlorine.
The <i>proto-chloride</i> , or sub-chloride	= 100	+ 14.715
The <i>per-chloride</i> (soluble)	= 100	+ 44.145

It is in the state of per-chloride that gold exists when dissolved by *aqua regia*.

The *sub-chloride* of gold, on adding water to it, is converted into one-third metallic gold, and two-thirds chloride. Acids, containing no water, do not produce any change on the sub-chloride; but dilute acids convert it into metallic gold and chloride of gold, the latter remaining in solution. Hence, by acting with acids on gold dissolved in *aqua regia*, we cannot obtain salts with base of oxide of gold, for the product, being a true chloride, contains no oxygen. For the same reason, sulphate or phosphate of soda, added to the solution, do not form sulphate or phosphate of gold. When sulphate or nitrate of silver is added to the chloride of gold, the whole of the sulphuric or nitric acid remains in the liquor, and a brownish yellow precipitate is formed, which is a mixture of chloride of silver and oxide of gold. The latter is taken up by muriatic acid. This precipitate, if dried and heated in a retort, yields oxygen gas by the decomposition of the oxide of gold.

A different view of this subject has, however, been taken by Dr. Thomson. He considers the product of dissolving gold in *aqua regia*, when carefully dried, not as a chloride, but as a *muriate* of the peroxide, and thinks its property of converting

protoxide into peroxide of iron to be strongly in favour of this supposition. His experiments tend to show that it is constituted of 2 atoms muriatic acid, + 1 atom of peroxide of gold, + 5 atoms of water. But such a constitution, it is obvious, must have been determined rather by the manner in which the facts are viewed, than from the direct evidence of analysis.

*Potassium and Sodium chlorides of gold.*—When pure potassa, not in excess, is added to liquid chloride of gold at common temperatures, no immediate precipitation ensues. After some time, however, or immediately if heat be applied, a very bulky reddish yellow precipitate appears, containing only five-sixths of the gold present in the chloride. An excess of alkali redissolves much of this precipitate; which is a *hydrated oxide of gold* with a little chloride. But if, instead of adding more alkali, the precipitate be well washed with water, and dried, it shrinks greatly in bulk, and a black powder remains which is not entirely soluble in muriatic acid.

If a considerable excess of potassa be mixed with the chloride of gold, the supernatant liquid acquires a light greenish yellow; and a blackish sediment is formed, in which not more than  $\frac{1}{10}$ th of the gold is found that was held in solution. The remaining  $\frac{9}{10}$ ths, united with oxygen, have combined with the potassa, which acts the part of a base, while the oxide of gold serves as a salifying principle. To this compound, Pelletier gives the name of *aurate of potassa*. Oxide of gold appears, therefore, adapted to unite with bases, rather than itself to form a base for combination with acids, with most of which it refuses to unite.

The precipitation of gold by a due quantity of potassa seems to be the effect of a double affinity, the chlorine passing to the potassium, and the oxygen of the potassa to the gold. Some chloride of gold remains undecomposed. When excess of potassa is used, the product is a mixture of chloride of potassium and aurate of potassa.

Baryta produces similar effects on chloride of gold, but seems to have a stronger affinity for the oxide.

When chlorides of potassium, sodium, or barium, are boiled with oxide of gold, the resulting liquid contains a mixture of aurate of alkali, and chloride of gold. The triple chloride of gold and sodium may also be prepared by dissolving 300 grains of gold in nitro-muriatic acid, adding 90 grains of dry common salt, and evaporating the solution. The triple salt crystallizes



in long four-sided prisms of a beautiful orange colour, which are not altered by exposure to the air. From Dr. Thomson's analysis they appear to consist of

Gold . . . . .	200	or of Bi-chloride of gold	272
Chloride of sodium ..	60	Chloride of sodium	60
Chlorine . . . . .	72	Water (8 atoms) .	72
Water . . . . .	72		
			404
	404		

*Iodide of gold* may be obtained by acting on oxide of gold with hydriodic acid, or by mixing chloride of gold with hydriodate of potassa, and washing and drying the precipitate. It is insoluble in cold water, and very sparingly soluble in hot. It is decomposed by heated nitric or sulphuric acids, which reduce the gold and set iodine at liberty. Liquid alkalis decompose it instantly, and it is decomposed by a temperature of 260° Fahr. It is constituted, according to Pelletier, of

Iodine . . . . .	34	. . . . .	100.
Gold . . . . .	66	. . . . .	194.1176
			100

*Bromide of gold.*—Balard observed the solubility of gold by bromine; and Lampadius found that the dry compound is constituted of equal parts of gold and bromine. It is of a greyish black colour, is soluble in water, and gives a deep red liquid, which yields crystallized hydro-bromate of gold by evaporation. The colour of this salt is so intense, that a single grain communicates a perceptible tint to 5000 grains of water. (Quart. Journ. July 1828.)

*Oxides of gold.*—The best process for obtaining *oxide of gold*, according to Pelletier, is to precipitate chloride of gold by magnesia. Muriate of magnesia is formed, which may be removed by washing, and the excess of magnesia may be dissolved by diluted nitric acid. In this case, the muriate of magnesia is doubtless converted into a chloride, and parts with its oxygen to the gold. The precipitate, at first a reddish yellow hydrate, must be dried at a very low heat, when it assumes a brownish black colour.

There is considerable disagreement as to the composition of the oxides of gold. Oberkampf deduces, as a mean of three experiments, that 100 parts of gold unite with 10.01 oxygen; Berzelius makes the proportion 12.07; and Javal, as nearly as

possible, the same. (Ann. de Ch. et de Ph. xvii. 337.) Pelletier, from the composition of the iodide, deduces the peroxide to consist of 100 gold + 10.03 oxygen; but besides this, he supposes that there is a protoxide containing only one-third of the oxygen which exists in the peroxide. Their composition, therefore, according to Pelletier, is as follows:

	Metal.	Oxygen.
Protoxide . . . . .	100 +	3.3495
Peroxide . . . . .	100 +	10.03

Mr. Dalton and Dr. Thomson have investigated the composition of oxide of gold by finding what quantity of protoxide of iron, as it exists in the sulphate, is converted into peroxide by precipitating a given weight of gold in solution. If we suppose the gold to be 100 grains, Mr. Dalton considers the nearest approximation to be, that it abandons 12.5 grains of oxygen to the protoxide of iron. (N. S. ii. 8.) The oxide of gold will consist then of 100 metal + 12.5 oxygen; and this oxide he regards not with Berzelius as the tritoxide, but as the protoxide.

Dr. Thomson dissolved 25 grains of gold in nitro-muriatic acid, and found that 104.25 grains of proto-sulphate of iron precipitated all the gold except 0.1 grain. But 104.25 of proto-sulphate of iron, in becoming per-sulphate, combine with 3 grains of oxygen, which must have been transferred from the gold, and  $25 : 3 :: 100 : 12$ , a result differing very little from those of other chemists.

*Atomic weight of gold.*—It will depend chiefly upon the theoretical view, taken of the oxide of gold, what number we assign as the equivalent of the metal. If we consider 12.5 of oxygen in 100 of gold to be the protoxide, the number 64, as already observed, must be the equivalent of gold. But if with Berzelius and Thomson, we regard 100 of gold + 12 oxygen as the tritoxide, the representative number of gold will be raised to 200. The latter number has been, also, deduced by Dr. Thomson from the triple chloride of gold and sodium. But if the gold in that compound be in the state of bi-chloride, we shall have the anomaly of a bi-chloride equivalent to a tritoxide, whereas in all well ascertained cases, the chlorides and oxides are similar atomic compounds. Notwithstanding, therefore, all that has been done on the subject, it cannot be admitted that we are yet in possession of the necessary data for determining the atomic weight of this metal.

*Fulminating gold.*—A solution of pure ammonia separates from the solution of gold in nitro-muriatic acid an oxide of gold, and a portion of ammonia, uniting with the oxide, forms a compound which detonates very loudly at a gentle heat, and is termed *fulminating gold*.

To obtain this compound, add a solution of ammonia in water, or the pure liquid ammonia, to diluted muriate of gold; a precipitate will appear, which will be redissolved if too much alkali be used. Let the liquor be filtered, and wash the sediment, which remains on the filter, with several portions of warm water. Dry it by exposure to the air, without any artificial heat, and preserve it in a bottle, closed, not with a glass stopper, but merely by a cork. A small portion of this powder, less than a grain in weight, being placed on the point of a knife, and held over a lamp, detonates violently. The precise temperature which is required is not known, but it appears to exceed  $250^{\circ}$  Fahr. At the moment of explosion, a transient flash is observed. The principal force is exerted downwards; and two or three grains, exploded on a pretty strong sheet of copper, will force a hole through it. Neither electricity, nor a spark from the flint and steel, are sufficient to occasion its detonation; but the slightest friction explodes it, and serious accidents have happened from this cause.

This detonation is explained as follows: Fulminating gold is an oxide of that metal, combined with ammonia. When its temperature is raised, the ammonia is decomposed; the hydrogen of the alkali unites with the oxygen of the oxide, and reduces the gold to a metallic state; and nitrogen gas, and probably aqueous vapour, are liberated in a highly expanded state. The violent impulse of these æriform products, on the surrounding atmosphere, appears to be the cause of the loud noise that is occasioned by the explosion of this compound. A similar explanation may be applied to other fulminating compounds of metallic oxides with ammonia; such as those of silver and mercury.

*Revival of gold from its solutions.*—The solution of chloride of gold is decomposed by certain combustible bodies, which appear to act by furnishing hydrogen to the chlorine, and reduce the gold to a metallic form, as in the following examples:

(a) Into a dilute solution of chloride of gold, contained in a glass jar, put a long narrow slip of charcoal, and expose the

whole to the direct light of the sun. The gold will be revived, and will appear on the charcoal in a metallic state, exhibiting a very beautiful appearance. The same change ensues without light, if the solution be exposed to a temperature of  $212^{\circ}$ .

(b) Moisten a piece of white taffeta riband, with the dilute solution of gold, and expose it to a current of hydrogen gas from iron filings, and dilute sulphuric acid. The gold will be reduced, and the riband will be gilt with the metal. By means of a camel's hair pencil, the gold may be so applied as to exhibit regular figures, when reduced.

(c) The same experiment may be repeated, substituting phosphureted hydrogen for common hydrogen gas. The reader, who wishes for a detail of various experiments of a similar kind, may consult an Essay on Combustion, by Mrs. Fulhame, published by Johnson, London, 1794; and also Count Rumford's paper, in the Phil. Trans., 1798, page 449.

(d) Several of the vegetable acids, but particularly the oxalic, decompose chloride of gold at common temperatures, especially if exposed to the sun's rays. The bin-oxalate of potassa is still more efficient; an effervescence arises from the escape of carbonic acid; and in about an hour, all the gold is revived. (Van Mons.) Tartaric acid does not produce the same effect, but bi-tartrate of potass occasions a decomposition, though less rapid. Acetic acid may be mingled with chloride of gold without producing any change.

(e) When a sheet of pure tin is immersed in a solution of nitro-muriate of gold, the oxide of gold is precipitated of a purple colour; and, when scraped off and collected, forms the *purple powder of Cassius*, much employed in enamelling. Or the metallic salt, largely diluted with water, may be put into a glass vessel with a few pieces of grain tin. In a short time, the liquor will become of the colour of red wine, and a very light flocculent precipitate will begin to appear, leaving the liquor clear. This, when well washed and dried, has a deep purple colour, and is the precipitate of Cassius. The same precipitate is obtained, by mixing a solution of gold with a recently made solution of tin in muriatic acid.

The composition and colour of the precipitates of gold, thrown down by muriate of tin at the minimum, have been shown, by Oberkampf, to be very variable. The colour approaches more to a violet, as the salt of tin bears a larger proportion to that of

gold; and the colour, communicated by the precipitate to porcelain, has the same variable character. When the muriate of gold is in excess, the precipitate has more of a rose colour. A violet compound was proved on analysis to contain 60 per cent. of oxide of tin, and 40 of metallic gold; and one of a fine purple consisted of  $20\frac{1}{2}$  oxide of tin and  $79\frac{1}{2}$  gold. The experiments of Macardieu, also, prove that in the purple precipitate, gold is in the metallic state. He formed it by acting with nitric acid upon an alloy of silver with  $\frac{9}{1000}$  of gold, and  $\frac{50}{1000}$  of tin, from which he obtained  $\frac{63}{1000}$  of purple precipitate. (Ann. de Ch. et de Ph. xxx. 147.)

(f) Gold is precipitated from its solvent by ether, but the oxide of gold is instantly redissolved by the ether, and forms the ethereal solution of gold. This solution is advantageously applied to the gilding of steel scissars, lancets, and other instruments, which it protects from rust with a very small expenditure of gold.

*Sulphuret of gold.*—When a current of sulphureted hydrogen gas is passed through a solution of gold in aqua regia, a black precipitate falls down which is a true *sulphuret of gold*. By the application of heat, the sulphur is expelled and the metal remains. The sulphuret is composed of

Gold .....	80.39	.....	100.
Sulphur .....	19.61	.....	24.39
	100.		124.39

Thus prepared, the sulphuret is more uniform in its composition, than that which is precipitated by alkaline hydro-sulphurets; for these contain sulphur in excess, which is thrown down along with the gold.

The sulphuret of gold is soluble in hydro-sulphuret of potassa. Liquid potassa takes up a part, and leaves a yellow powder, which is metallic gold. The alkaline hydro-sulphurets do not dissolve gold, however minutely divided, till sulphur is added, when probably a sulphuret of gold is formed, on which the hydro-sulphuret is capable of acting.

*Phosphuret.*—Gold may be combined with phosphorus, either by precipitating its solution with sulphureted hydrogen, or, as Mr. E. Davy discovered, by heating finely divided gold with phosphorus in a tube deprived of air. It has a grey colour,

and a metallic lustre; is decomposed by the heat of a spirit lamp; and contains about 14 per cent. of phosphorus.

The *methods of purifying gold*, by the operations of *cupelling* and *quartation*, would lead into too long details. They are very perspicuously described by La Grange, in the 44th chapter of his Manual; and in Aikin's Chemical Dictionary, article Gold. To the latter work; to Lewis's Philosophical Commerce of the Arts; and to Mr. Hatchett's paper, in the Philosophical Transactions for 1803, I refer also for much valuable information respecting the alloys of gold with other metals. It may be proper, however, to observe that gold, which is too soft, in its pure state, for many purposes, that of coin for instance, has its hardness greatly increased, without any injury to its colour, by being melted or alloyed with a small proportion of copper. Sterling or standard gold consists of gold alloyed with  $\frac{1}{3}$  of silver, copper, or a mixture of both, as is most common in British coin. Its specific gravity has varied in the coin of different reigns, as Mr. Hatchett has shown by a Table printed in his memoir. As a general average, in British coins, it may be stated at 17.5. It is a singular fact, that some kinds of copper, which do not themselves appear defective in any respect, totally destroy the ductility of gold. This appears to be owing to the contamination of the copper with a very small quantity of lead and antimony, of either of which metals only about  $\frac{1}{1920}$ th in weight is sufficient to produce this injurious effect.

The degree of purity of gold is expressed by the number of parts of that metal, contained in 24 parts of any mixture. Thus, gold, which in 24 such parts (termed *carats*), contains 22 of the pure metal, is said to be 22 carats fine. Absolutely pure gold, using the same language, is 24 carats fine; and gold alloyed with an equal weight of another metal, 12 carats fine.

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## SECTION XXXVI.

### *Platinum.*

Platinum, in the state in which it reaches this country, is generally accompanied by variable proportions of iridium, rhodium, palladium, iron, copper, and mercury, and is mixed also

with sand. It had been discovered in no other places than Choco and Santa Fé, in South America, until Vauquelin, a few years ago, detected it unaccompanied by iridium, rhodium, or osmium, in some grey silver ores from Estremadura; and it has been since brought from St. Domingo, from the gold mines of Brazil, and from the Uralian mountains. (Phil. Mag. Nov. 1827.) The general aspect of the ore of platinum is that of small grains or scales, of a whiter colour than iron, and extremely heavy. Their usual size does not exceed a line in diameter. Humboldt describes a few specimens of platinum either seen by himself or by persons of good authority, of several thousand grains each in weight. (Ann. de Ch. et de Ph. xxxvii. 222.) Its usual situation is in alluvial ground, and we are indebted to Boussingault for tracing it to its native source in a decomposing syenite at Santa Rosa, in Mexico, nearly 3500 feet above the level of the sea. (Id. xxxii. 209.)

Various processes have been contrived for extracting and purifying platinum, but it is no longer necessary to describe them, since we have been recently put in possession of the method of extracting platinum and rendering it malleable, so long and successfully practised by the late Dr. Wollaston. (Phil. Trans. 1829.)

With regard to the proportions of muriatic and nitric acids employed to dissolve the crude ore, Dr. Wollaston recommends that the nitric acid should be the *single aqua-fortis* of commerce, the sp. gr. of which varies from 1.190 to 1.200. In round numbers, muriatic acid equivalent to 150 marble, and nitric acid equivalent to 40 marble, will take 100 of crude platinum; but in order to avoid waste of acid, and also to render the solution purer, there should be, in the menstruum, a redundancy of at least 20 per cent. of the ore.\* The materials should be allowed to digest, three or four days, with a heat which ought gradually to be raised. The solution, being then

\* The quantity of *real* muriatic acid, which is equivalent to a given weight of marble, may be learned by applying the rule, stated vol. i. p. 296; and that of *real* nitric acid, by the rule vol. i. p. 352. It is easy, then, from the Table of the real acid in acids of different specific gravities, to calculate how much liquid acid of the density we mean to employ, represents the real acid required. For example, 150 marble = 111 real muriatic acid; and supposing we are about to use muriatic acid of sp. gr. 1.162, we find (p. 290) that 100 grs. of such acid contain 33.945 real; therefore 33.945 : 100 :: 111 : 326, very nearly.

poured off, should be suffered to stand until a quantity of fine pulverulent ore of iridium, suspended in the liquid, has completely subsided, and it should then be mixed with 41 parts of sal ammoniac dissolved in about five parts of water. The first precipitate, which will thus be obtained, will weigh about 165 parts, and will yield about 66 parts of pure platinum. The mother liquid will still contain about 11 parts of platinum. These, with some of the other metals yet held in solution, are to be recovered by precipitation from the liquor with clean bars of iron: and the precipitate is to be redissolved in a proportionate quantity of aqua regia, similar in its composition to that above directed. But in this case, before adding sal ammoniac, about 1 part by measure of strong muriatic acid should be mixed with 32 parts by measure of the nitro-muriatic solution, to prevent any precipitation of palladium or lead, along with the ammonia-muriate of platinum.

The yellow precipitate must be well washed, in order to free it from the various impurities, which are known to be contained in the complicated ore in question; and must ultimately be well pressed, in order to remove the last remnant of the washings. It is next to be heated with the utmost caution in a black-lead pot, at so low a heat as just to expel the whole of the sal ammoniac, and to occasion the particles of platinum to cohere as little as possible, for on this depends the ultimate ductility of the product.

Platinum, thus extracted from its ore, is fit for all chemical purposes; but further operations, chiefly of a mechanical nature, are necessary to adapt it for being formed into malleable and ductile masses. These consist in pulverization in a wooden mortar with a wooden pestle, and subsequent washing, shaking, and decanting. We thus obtain a fine powder or *mud*, which is put into a hollow brass cylinder, stopped at one end by a plug, in such a manner at first as to allow the moisture to drain off. It is then, by means of a piston, subjected to strong compression carefully applied, and being now firm enough to bear handling, it is heated to redness, on a charcoal fire, by which moisture and other volatile matters are driven off, and it acquires greater cohesion. It is next strongly heated, and afterwards forged into ingots, which are cleared from impurities by smearing their surface with a moistened mixture of equal parts, by measure, of crystallized borax and common salt of tartar, which when in fusion



is a ready solvent of such impurities, and then exposing the ingots upon a platinum tray under an inverted pot, to the heat of a wind furnace. The ingot, on being taken out of the furnace, is immediately to be plunged into dilute sulphuric acid, which, in the course of a few hours, will entirely dissolve the flux left adhering to the surface. The ingots may be flattened into leaf, drawn into wire, or submitted to any of the processes, of which the most ductile metals are capable.

Platinum has the following properties :

It is a white metal, resembling silver in colour, but greatly exceeding it, and indeed all other metals, in density.

Dr. Wollaston found the sp. gr. of a button which had been melted by Dr. Clarke under the oxy-hydrogen blow-pipe, to be 21.16. The mean sp. gr. after forging is about 21.25; that of some rods, after being drawn is 21.4; and that of fine platinum wire is 21.5, which may be considered as the maximum sp. gr. of which this metal is capable. To estimate its tenacity, Dr. Wollaston ascertained the weight required to break platinum wires of different diameters. Taking 590 pounds, as determined by 11 consecutive trials, to be the measure of the tenacity of platinum prepared by his process, and considering that the tenacity of gold wire reduced to the same standard is about 500, and that of iron wire 600, those numbers will express the relative tenacities of the three metals.

When two pieces of platinum wire are divided with a sharp tool in a slanting direction, and, being then heeded to redness, are struck with a hammer upon an anvil, so as to force into contact the newly divided surfaces, they become firmly welded together. But any degree of burnishing prevents the welding from being effected. The elasticity of the metal has been said to be sufficient to fit it for making the pendulum springs of watches.

Platinum is extremely difficult of fusion. It may be melted, however, by the blow-pipe, with the aid of oxygen gas. A globule, weighing 29 grains, boiled violently in the focus of a lens about three feet in diameter (69 Ann. de Chim. p. 93), and Dr. Clarke, by means of the blow-pipe with compressed oxygen and hydrogen gases, has kept more than 200 grains of platinum in a boiling state for some time.

Platinum was found by Dr. Wollaston to be a remarkably slow conductor of caloric. When equal pieces of silver, copper, and platinum, covered with wax, were heated at one end, the

wax was melted  $3\frac{1}{2}$  inches on the silver;  $2\frac{1}{2}$  on the copper; and 1 inch only on the platinum. Its expansion by heat is considerably less than that of steel; which, between the temperatures of  $32^{\circ}$  and  $212^{\circ}$ , is expanded about 12 parts in 10,000, while the expansion of platinum is only about 10.

It is not oxidized by the long-continued and concurrent action of heat and air. To obtain its oxides, it is necessary first to combine it with chlorine, either by the direct action of that element in the state of gas or of watery solution, or by dissolving platinum in nitro-muriatic acid. One part of the pure laminated metal may be digested with sixteen parts of nitro-muriatic acid in a glass matrass; nitrous gas is evolved; and a deep red solution is obtained. From this the excess of acid may be expelled by evaporating to dryness at a very gentle heat. The residue is the *per-chloride* of platinum; and this, when heated at the temperature of melting lead, is converted into the *proto-chloride* which, when the heat has been properly regulated, and continued long enough, is insoluble in water. But if not sufficiently heated, the residue dissolves partially in water, and forms an almost opake liquid, which is a solution of proto-chloride and per-chloride. On evaporating this mixed fluid, a brown powder precipitates, which, though more soluble than proto-chloride in water and in muriatic acid, is in fact only that compound in a more finely divided state. The proto-chloride, according to Magnus (Ann. de Ch. et de Ph. xl. 110) is composed of 26.41 chlorine + 73.59 metal. Supposing it to be constituted of an atom of each element, the equivalent number of platinum would by these data be 100; by others it is nearer 96.

The proto-chloride may also be separated from the per-chloride by the repeated affusion of cold water, which takes up the latter almost exclusively. The proto-salt dissolves in muriatic acid; and if to this solution we add chloride of potassium, we obtain a red salt in prismatic crystals, consisting of an atom of chloride of potassium and an atom of proto-chloride of platinum. This salt is soluble in water, but not in alcohol. Double compounds of proto-chloride of platinum, with chloride of sodium and muriate of ammonia, may also be obtained.

A third chloride has been supposed to exist, chiefly on probable evidence derived from Mr. E. Davy's experiments on the oxides. Berzelius, in his late elaborate memoir, has expressed an opinion favourable to the existence of this *sesqui-chloride*,

chiefly because he has observed an analogous compound of rhodium and chlorine. At present, however, it must be considered as not sufficiently established.

Per-chloride of platinum, as existing in the nitro-muriatic solution, may be crystallized by careful evaporation. The salt has a very acrid taste, and is deliquescent. Its solution in water is not precipitated by ferro-prussiate of potassa, nor by sulphate of iron, if free from other metals. It is precipitated by the gallic acid as present in tincture of galls, of a dark green colour, which becomes gradually paler by standing.

The most delicate test of the presence of platinum is muriate of tin. A solution of platinum, so dilute as to be scarcely distinguishable from water, assumes a bright red colour, on the addition of a single drop of the recent solution of tin. Professor Silliman recommends hydriodic acid as the best test for platinum. When dropped into a weak solution of that metal, it almost instantly produces a deep wine-red colour, or reddish brown, which on standing becomes very intense. No other metallic solution gave similar results with that acid. Iodide of potassium, with the addition of a little dilute sulphuric acid, renders a solution containing 1-10,000th of chloride of platinum at the first moment browner, afterwards dark green, and finally a black precipitate ensues. (Quart. Journ. N. S. iii. 378.)

Per-chloride of platinum has the property of being precipitated by a solution of muriate of ammonia. By this character, platinum is distinguished from most other metals, and may be separated when mingled with them in solution. The precipitate, thus obtained, is decomposed by a low red heat, and leaves pure platinum in a light spongy form, in which state it is well adapted to act upon mixtures of oxygen with hydrogen and other gases. (See vol. i. p. 259.) If pure platinum be wanted, the solution should be at least twice repeated; for the precipitate first formed contains a small proportion of any other metal that may happen to be present. The ammonia muriate consists, according to Dr. Thomson, of

2 atoms of chlorine ..	72	}	168
1 atom of platinum ..	96		
1 atom of sal-ammoniac . . . .			54

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Fischer describes three of these ammonia-muriates of plati-

num. That which is well known, he considers as the neutral salt,—another, which is white, contains an excess of ammonia;—and a third, which is yellow, contains an excess of oxide of platinum. (Quart. Journ. March 1829, p. 193.)

*Potassa-perchloride.*—When pure potassa is poured into the solution of per-chloride of platinum, a precipitate ensues, which is not an oxide of platinum, but a chloride, or, according to Dr. Thomson, a compound of 1 atom of bi-chloride of platinum, and 1 atom of chloride of potassium. With soda also, it forms a triple combination, or *soda-perchloride*. This is best obtained, by adding to nitric acid, in a retort, platinum, with twice its weight of common salt, and applying heat till about four-fifths of the fluid have come over. The remaining liquor forms, on cooling, fine prismatic crystals, sometimes four or five inches long; and either reddish brown, like titanium; yellow, like amber; or of a beautiful coquelicot colour. This salt may be considered either as a compound of

1 atom bi-chloride of platinum .....	168
1 atom chloride of sodium .....	60
8 atoms of water .....	72
	200

*Oxides of platinum.*—Berzelius describes two oxides of platinum equivalent to the two chlorides. The first is obtained from the proto-chloride, by acting upon it with an excess of potassa or soda. (87 Ann. de Chim. p. 126.) The protoxide is black, and consists of

Platinum .....	92.35	....	100.
Oxygen .....	7.65	....	8.287
	100.		108.287

The peroxide, he conceives to have been obtained only in combination, but Vauquelin attests that the oxide, precipitated from the per-chloride by soda, is constituted of proportions, which would class it as a peroxide. (Ann. de Ch. et de Ph. v.) It consists, according to Berzelius, of

Platinum .....	85.93	....	100.
Oxygen .....	14.07	....	16.38
	100.		116.38

A third oxide has been described by Mr. E. Davy, which appears to be intermediate between the peroxide and the protoxide. It was formed by boiling together strong nitric acid and fulminating platinum, drying the product, and heating it just below redness; then washing with water, and, finally, with a little potassa. Its colour was dark iron-grey; it was not affected by water, either hot or cold; nor by nitrous, sulphuric, or phosphoric acid; it was insoluble by nitro-muriatic acid, and by muriatic acid, unless when heated. It was shown, by analysis, to contain

Platinum . . . . .	89.366	. . . .	100.
Oxygen . . . . .	10.634	. . . .	11.9
			100.

The *sub-oxide* of platinum, which Mr. Cooper obtained by precipitating the chloride with protonitrate of mercury and applying no more heat than was judged sufficient to expel the calomel, was composed of 100 metal + 4.517 oxygen. (Quart. Journ. vol. iii.) But it has been objected by Berzelius and E. Davy, that the temperature necessary to sublime calomel is sufficient to expel part of the oxygen from the oxide, and therefore that when prepared in this way, it cannot be regarded as a definite compound.

The oxygen in the three oxides, appears then to be nearly in the proportion of 8, 12, and 16, to 100 of the metal. Assuming Berzelius's analysis of the first oxide to be correct, the equivalent number deducible for platinum will be 96.5. Dr. Thomson, from other considerations, is induced to fix it at 96; but the subject requires more accurate investigation, before we can assign with confidence, the equivalent number of this metal.

*Sulphurets.*—The per-chloride of platinum is decomposed by sulphureted hydrogen, and a black powder is obtained, which becomes reddish brown with an excess of the precipitant, but reassumes its black colour, on exposure to the air. (Berzelius.) Its composition cannot be investigated easily, for the sulphur passes so rapidly to the state of sulphuric acid, as, during the desiccation of the powder, to destroy the paper on which it is collected. Vauquelin asserts that it is not a simple sulphuret, but a *hydro-sulphureted oxide of platinum*. (Ann. de Chim. et de Phys. v. 263.) It is more probable, however, that it is a bi-sulphuret.

The direct combination of platinum and sulphur for which useful directions have been given by Mr. Faraday (Manip. sect. 688), was found by Mr. E. Davy to give an infusible black powder, containing about 16 parts of sulphur to 100 metal. (Phil. Mag. vol. 40.) Vauquelin formed the sulphuret by heating 10 parts of the triple muriate of ammonia and platinum with 20 parts of sulphur, or by a similar treatment of one part of finely divided platinum, with two of sulphur. He agrees with Mr. Davy as to the proportions of its elements.

*Sulphate.*—From the sulphuret, the *sulphate of platinum* is best prepared by the action of nitric acid. It is soluble in water, in alcohol, and ether; and the first-mentioned solution, Mr. Davy finds to be the best test yet tried for discovering gelatine.

The action of alcohol on sulphate of platinum occasions the formation of a substance, which is possessed of very singular properties. Equal volumes of a strong aqueous solution of this sulphate and of alcohol, heated together, deposit a black powder, which, after being welledulcorated, and dried at a very gentle heat, exhibits the following properties: It is black and in small lumps, which are soft to the touch, and easily reduced to an impalpable powder. This powder is tasteless, and insoluble in water either hot or cold. When gently heated on a slip of platinum, a feeble explosion takes place, accompanied with a hissing noise, and a flash of red light, and the platinum is reduced. Brought into contact with ammoniacal gas, it becomes red-hot, and scintillates. It is instantly decomposed by alcohol, as is shown in a very striking manner by moistening paper, sand, cork, or sponge, with that fluid, and placing the smallest particle of the powder on them. It hisses, and becomes red-hot; and Mr. E. Davy, to whom we owe its discovery, proposes it as an excellent means of kindling a match. It appears to consist of  $96\frac{1}{4}$  per cent. platinum, with some nitrous acid, a little oxygen, and a very minute proportion of carbon. The nitrous acid is accounted for, by the peculiar way in which the sulphate had been formed. (Phil. Trans. 1820.)

*Phosphuret.*—Phosphorus and platinum may be united, either by passing phosphureted hydrogen into a solution of the metal; or, according to Mr. E. Davy, they combine directly in exhausted tubes with vivid ignition. The result is a bluish grey powder, infusible, and consisting of 17 phosphorus to 100 of metal.

Platinum is acted upon when fused with *nitrate of potassa*, or with *nitrate of soda*, and also with *pure fixed alkalis*. The latter property limits the utility of platinum as a material for crucibles, or other chemical vessels, to processes in which alkalis are not employed.

*Fulminating Platinum*.—A fulminating compound of platinum, analogous in its composition and properties to *fulminating gold*, has been prepared by Mr. E. Davy, by precipitating a solution of sulphate of platinum with a slight excess of pure ammonia. (Phil. Trans. 1817.) The precipitate, thus obtained, was washed, and dried sufficiently to separate it from the filter. It was then put into a Florence flask with a solution of pure potassa, and the fluid boiled nearly to dryness. A quantity of water was then added, and the solid matter, after being well washed, was dried for several days at the temperature of 212° Fahrenheit. The powder, thus prepared, has different shades of colour, from a light brown to a dark chocolate, and even almost black. One grain, laid on a thin sheet of copper, and heated to 400° or 420° Fahrenheit, produces a report louder than that of a pistol, and the copper is deeply indented. Like fulminating gold, it is incapable of being exploded by percussion. It appears to be a triple compound of oxide of platinum, ammonia, and water.

A compound possessing similar properties has been formed by Zeize. One part of chloride of platinum, and twelve of alcohol, s. g. 0.813, are to be heated gently together in a retort, till the chloride becomes black, and the liquid clear and colourless. The fluid being decanted, the precipitate is to be washed with warm water until all acid is removed, and then carefully dried. When moderately heated, with or without the access of air, it inflames, decrepitates slightly, and yields carbonic acid, oxygen, and water, with a little acetic acid. (Quart. Journ. July 1828.)

*Alloys of platinum*.—Platinum enters into combination with other metals, and composes alloys, which are not, in general, characterized by useful properties. Its affinity for lead is strikingly shown by the following experiment: If a piece of lead foil, and another of platinum foil, of equal dimensions, be rolled up together, and the flame of a candle be cautiously directed by a blow-pipe towards the edges of the roll, at about a red heat, the two metals will combine with a sort of explosive force, scattering their melted particles, and emitting light and

heat in a surprising manner. (Ann. of Phil. xiv. 230.) A small bit of tin, zinc, or antimony, rolled in platinum leaf, and treated in like manner, exhibits similar appearances.

With potassium and sodium, platinum affords brittle compounds. In the proportion of 1-16th, it renders gold pale, and when it amounts to 1-6th the colour of the alloy differs very little from that of platinum. It readily amalgamates with mercury, and diminishes the fusibility of the fusible metals. When alloyed with the more oxidable metals, it is remarkable that platinum becomes soluble in nitric acid, which has no action on the pure metal.

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## SECTION XXXVII.

### *Rhodium and Palladium.*

These two metals were discovered by Dr. Wollaston, who first separated them from the ore of platinum. They have since been the subjects of an elaborate set of experiments by Berzelius, whose memoir throws considerable light on their properties and combinations. (Ann. de Ch. et de Ph. Jan. 1829.)

I. RHODIUM. When a solution of the ore of platinum in nitro-muriatic acid has been precipitated, as far as possible, by muriate of ammonia (see sect. 36), it still retains considerable colour, varying with the strength and proportion of the acids that have been employed for effecting the solution. Beside much iron, and a little of the ammonia-muriate of platinum, it contains, also, other metals in very small proportion, which Dr. Wollaston separated as follows:

Let a cylinder, or thin plate of zinc, or iron, be immersed in the solution. It will throw down all the metals in the state of a black powder. Wash the precipitate (without drying it) with very dilute nitric acid, assisted by a gentle heat, which will dissolve the copper and lead. Digest the remainder in weak nitro-muriatic acid; and to the solution, when completed, add a portion of muriate of soda, equivalent in weight to about one fiftieth the ore of platinum employed. Evaporate by a very gentle heat. The dry mass contains the soda-muriates (or soda-chlorides) of platinum, palladium, and rhodium; the two former of which may be separated by alcohol, and the salt of rhodium will remain. Dissolve it in a small quantity of hot



water, allow it to crystallize, and redissolve the crystals. From their solution the rhodium may be precipitated by zinc, which throws down a black powder, amounting, in weight, to one grain from 100 of the ore.

The soda-muriate of rhodium forms rhomboidal crystals of an intensely deep red colour. From the solution of this compound salt, ammonia after a while causes a lemon-yellow precipitate, which is a compound of oxide of rhodium with ammonia. This, when exposed to heat, continues black; with borax it acquires a white metallic lustre, but appears infusible by any degree of heat. It is rendered fusible by arsenic, and also by sulphur, both of which may be expelled by a continued heat; but the metallic button, thus obtained, is not malleable.

The specific gravity of rhodium, as near as it could be taken by Dr. Wollaston, was 11. By a very intense heat, produced in a wind furnace, Messrs. Stodart and Faraday succeeded in effecting its fusion.

When heated to redness with free access of air, it is converted into a black oxide; 100 parts of the metal, which has been reduced by hydrogen gas, become 117.9 grains. By a still higher degree of heat, the oxygen, which it had acquired, is expelled, and it is therefore entitled, equally with mercury and nickel, to rank among the noble metals. (Berzelius.)

Rhodium unites readily with all the metals that have been tried, excepting mercury. It does not discolour gold, when alloyed with it, in which respect it differs both from platinum and palladium. Its alloy with steel has been described in section 16.

Rhodium resists the action of acids, even of the nitro-muriatic. But Berzelius finds that it is rendered soluble in the last mentioned acid, by previous fusion with bi-sulphate of potassa, a property of the greatest use in analysis, because it enables us to separate very minute quantities of rhodium from iridium and osmium.

The great hardness of rhodium renders it very difficult to pulverize. Berzelius triturated it with chloride of potassium or sodium, and exposed the powder, heated, to a current of chlorine gas for some hours. The red saline mass was dissolved in a very small quantity of hot water, and precipitated by alcohol, and then washed with alcohol of sp. gr. .840. The result was the soda-chloride, or potassa-chloride, already described.

Rhodium is also acted upon when exposed *per se* to a current of chlorine. Two sublimate are found in the tube, the one yellow, the other red, which are both chlorides, but with different proportions of elements. The red powder boiled with potassa gives an oxide which, with heated muriatic acid, yields a red solution, and a powder of a sullied violet colour. The latter is the *proto-chloride*. Berzelius is induced to believe that the red salts of rhodium are not equivalent to per-chloride of platinum, but to a chloride, intermediate between the proto-chloride and per-chloride of platinum, first pointed out by E. Davy. There appear then to be three chlorides, composed of 1 atom of rhodium with 1, 2, and 3 atoms of chlorine respectively; but no chloride is known with 4 atoms of chlorine.

Three oxides of this metal, were formerly described by Berzelius (Ann. of Phil. iii. 252); but he is now of opinion that the black oxide, formed by heat, is not the true protoxide, but a mixed or compound oxide. Decomposition of the soda-chloride by sulphurous acid gives the protoxide, which, like that of copper, has a strong tendency to resolve itself into metal, and peroxide. He describes also a hydrate containing 75.9 rhodium, 17.5 oxygen, 6.6 water. The oxide and the hydrate are decomposed by hydrogen gas, without requiring any other heat than that produced by the reduction.

When an alloy of silver or gold with rhodium is digested in nitric or nitro-muriatic acid, the rhodium remains untouched; but, when alloyed with three times its weight of bismuth, copper, or lead, each of these alloys may be dissolved completely, in a mixture, by measure, of two parts muriatic acid with one of nitric. Lead appears preferable, as it forms, by evaporation, an insoluble chloride. The chloride of rhodium then exhibits the rose colour, from which the name of the metal has been derived. It is soluble in alcohol.

Rhodium is not precipitated from its solution by ferro-prussiate of potassa, nor by muriate of ammonia, nor by hydro-sulphuret of ammonia. The carbonated alkalis produce no change; but the pure alkalis precipitate a yellow oxide, soluble in all acids that have been tried.

Dr. Thomson considers the existence of two oxides of rhodium as established, the black or protoxide, and the yellow, which are constituted as follows:

	Metal.	Oxygen.	Metal.	Oxygen.
The protoxide . . . . .	100	+ 18.2	or 44	+ 8
The peroxide . . . . .	100	+ 36.4	or 44	+ 16

Whether the brown oxide be a distinct compound, or admixture of the black and the yellow oxides, he has not ascertained. If these proportions be correct, 44 will be the atomic weight of rhodium, 52 that of the protoxide, and 60 of the peroxide. The oxy-salts of rhodium are scarcely known. They are best prepared by acting with acids on the precipitate by carbonate of soda from solution of the soda chloride.

II. PALLADIUM. The alcoholic solution (I.) contains the soda-chlorides of palladium and platinum. The latter metal may be precipitated by muriate of ammonia; and palladium may be obtained from the remaining liquid, by the addition of prussiate of potassa, which occasions a sediment, at first of a deep orange colour, and changing afterwards to a dirty bottle-green, owing, probably, to the presence of iron. The precipitate is to be ignited, and purified from iron, by cupellation with borax.

A more simple method of obtaining palladium has since been described by Dr. Wollaston. To a solution of the ore of platinum in nitro-muriatic acid, neutralized by evaporating the redundant acid, or by adding an alkali, and either before or after the separation of the platinum by muriate of ammonia, let prussiate of mercury be added. In a short time the liquid becomes yellow, and a flocculent precipitate is gradually formed, of a pale yellowish white colour, which is the prussiate of palladium. This, after being dried, is to be combined with sulphur, and each cake of the sulphuret, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little nitre. The sulphuret is then to be roasted, at a low red heat, on a flat brick, and, when reduced into a pasty consistence, pressed into a square or oblong and perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface. During this process, sulphur flies off in the state of sulphurous acid, especially at those moments when the heat is allowed occasionally to subside. The ingot is then to be cooled, and, when cold, is to be tapped with a light hammer, in order to condense and beat down the spongy excrescences on its surface. The alternate roastings and gentle hammerings require the utmost

patience and perseverance before the cake can be brought to bear hard blows, but it may by these means at length be made so flat and square, as to bear being passed through the flattening-mill, and so laminated to any required degree of thinness. Thus prepared, it is always, however, brittle while hot, probably owing to its containing a remnant of sulphur. (Phil. Trans. 1829.)

On examining some ore of platinum, brought from the gold mines of Brazil, Dr. Wollaston discovered in it small fragments of *native palladium*, which appear to be free from admixture with every other metal, except a very minute portion of iridium. These fragments differ from the grains of platinum in being formed of fibres, which are in some degree divergent from one extremity. This external character Dr. Wollaston deems sufficient for distinguishing the metal, in situations where recourse cannot be had to experiment. (Phil. Trans. 1809.) Mr. Cloud, assayer-master of the American mint, has also discovered palladium in a native alloy of gold with that metal. (74 Ann. de Chim. 99.) The alloy contained no other metal, and was perfectly free from its common ingredients, copper and silver. The largest mass of native palladium, which is on record, is a bar exhibited at the Royal Institution in Feb. 1826. It weighed upwards of six-pounds, and had been received from the province of Sergipe, in the Brazils.

The following are the properties of palladium :

Its colour resembles that of platinum, except that it is of a duller white. It is malleable and ductile. Its specific gravity varies from 10.972 to 11.482. Its power of conducting caloric is nearly equal to that of platinum, which it rather surpasses in expansibility by heat.

Exposed in an open vessel, to a greater degree of heat than is required to melt gold, no oxidizement ensues ; and no degree of fusion takes place. On increasing the fire considerably, a melted button is obtained, and the specific gravity is increased to 11.871. The metal, in this state, has a greyish white colour. Its hardness exceeds that of wrought iron. By the file it acquires the brilliancy of platinum, and is malleable to a great degree.

Berzelius finds two oxides of palladium. (Ann. de Ch. et de Phys. Jan. 1829.)

	Protoxide.	Peroxide.
Palladium . . . . .	86.94 . . . . .	76.92
Oxygen . . . . .	13.06 . . . . .	23.08
	100.	100.

Palladium, exposed in a state of fine division, and heated to redness, to oxygen gas, becomes blue, but its weight is scarcely increased. It is less easily oxidized by fusion with potash or nitre, than any of the other metals that accompany platinum. The oxide, which is thus formed, is the protoxide. It is more easily obtained by heating the per-chloride, mixed with sub-carbonate of soda, to a little below redness. The per-chloride, upon which caustic or carbonated soda is poured, becomes gelatinous, and deposits a hydrated peroxide, which becomes black on raising the liquid to the boiling point. The protoxide, even when humid, dissolves very slowly in acids; and its salts have not been sufficiently investigated.

Palladium readily combines with sulphur. The compound is whiter than the separate metal, and is very brittle. It has been investigated by Berzelius, and shown to be composed as follows:

Palladium . . . . .	78.03 . . . . .	100.
Sulphur . . . . .	21.97 . . . . .	28.15
	100.	128.15

The equivalent number for the metal, deducible both from the oxide and sulphuret, is 56.2. We may, therefore, denote the weight of its atom by 56; that of the oxide by 64; and of the sulphuret by 72.

Palladium unites with potassa by fusion, and also with soda, but less decidedly. Ammonia, allowed to stand over it for some days, acquires a bluish tinge, and holds in solution a small portion of oxide of palladium.

Sulphuric acid, boiled with palladium, acquires a beautiful blue colour, and dissolves a portion of the metal. The action of this acid, however, is not powerful; and it cannot be considered as a fit solvent for palladium. Nitric acid acts with much greater energy on palladium. It oxidizes the metal with somewhat more difficulty than it acts on silver; and, by dissolving the oxide, forms a very beautiful red solution. During this process no nitrous gas is disengaged. Nitrous acid has a

more rapid action on palladium than the nitric. From these solutions, potassa throws down an orange-coloured precipitate, which is probably a hydrate. Muriatic acid, by being boiled on palladium, acts upon it, and acquires a beautiful red colour.

But the appropriate solvent of palladium is nitro-muriatic acid, with which it yields a beautiful red solution. This solution, according to the recent experiments of Berzelius, contains much proto-chloride of palladium, and nitrate of protoxide, and also a little per-chloride, the last of which is decomposed by heat, and causes the odour of chlorine. By adding chloride of potassium or of sodium to the solution, we obtain the potassa-chloride, or soda-chloride of palladium, in which the palladium is united with one proportion of chlorine. This salt is readily soluble in water and in alcohol, and the alcoholic solution is decomposed by boiling, or by sulphurous acid, which precipitate the protoxide. The per-chloride is formed by dissolving the above salt in nitro-muriatic acid and evaporating. It is not soluble in alcohol, nor is its solution in water decomposed by heat.

From all the solutions of palladium in acids, a precipitate may be produced by alkalis and earths. These precipitates are mostly of a fine orange colour; and are partly dissolved and decoloured by the alkalis. That occasioned by ammonia, when redissolved, has a greenish blue colour; but this, according to Berzelius, is owing to the presence of copper. If to the solution of 56 grains of palladium, a quantity of carbonate of potassa be added, containing 48 grains of base, we obtain on evaporation extremely minute prismatic crystals, of a beautiful brown colour, and a sweet astringent taste, insoluble in alcohol, but pretty soluble in water. (Thomson.) Sulphate, nitrate, and muriate of potassa, produce an orange precipitate in the salts of palladium, as in those of platinum; but the precipitates from nitrate of palladium have generally a deeper shade of orange. All the metals, except gold, platinum, and silver, cause very copious precipitates in solutions of palladium. Recent muriate of tin produces a dark orange or brown precipitate from neutralized salts of palladium, and is a very delicate test of this metal. Green sulphate of iron precipitates palladium in a metallic state; and, if the experiment succeed, the precipitate is about equal in weight to the palladium employed. Ferro-prussiate of potassa causes an olive-coloured precipitate.

The prussiate of palladium, separated by a neutral solution of prussiate of mercury, has the property, when heated to about 500° of Fahrenheit, of detonating, with a noise similar to that occasioned by firing an equal quantity of gunpowder. Hydro-sulphurets, and water impregnated with sulphureted hydrogen gas, occasion a dark brown sediment from solutions of palladium.

Palladium readily combines with other metals. It has the property, in common with platinum, of destroying the colour of gold, even when in a very small proportion.—Thus one part of platinum, or palladium, fused with six of gold, reduces the colour of the gold nearly to that of the white metal employed.

Dr. Wollaston has furnished an alloy of gold and palladium for the graduation of the magnificent circular instrument, constructed by Mr. Troughton, for the Greenwich observatory. It has the appearance of platinum, and a degree of hardness, which peculiarly fits it for receiving the graduations.

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## SECTION XXXVIII.

### *Iridium and Osmium.*

When the ore of platinum has been submitted to the action of nitro-muriatic acid, a part remains undissolved, in the form of a black powder, resembling plumbago. In this substance, the late Mr. Smithson Tennant discovered two new metals. (Phil. Trans. 1804.) These have since been investigated by Vauquelin (Ann. de Ch. vol. 89), and by Berzelius (Id. Feb. 1829). The process employed by Mr. Tennant to separate them was the following:

I. 1. The powder was fused in a silver crucible with pure soda, and the alkali then washed off with water. It had acquired a deep orange or brownish yellow colour, but much of the powder was undissolved. The residue was digested in muriatic acid, and a dark blue solution obtained, which afterwards became of a dusky olive-green; and, finally, by continuing the heat, of a deep red colour. By the alternate action of the acid and alkali, the whole of the powder appeared capable of solution.

2. The alkaline solution contained the oxide of a volatile

metal not before described; and also a small portion of another metal. When the solution was kept some weeks, the latter metal separated spontaneously in thin dark-coloured flakes. The acid solution contained both metals also; but principally one, which is not altered by muriate of tin, is precipitated of a dark brown colour by pure alkali; and which exhibits, during solution in muriatic acid, a striking variety of colours, arising from variations in its degree of oxidation. From this property Mr. Tennant termed it IRIDIUM. The proportion of oxygen in its oxide was not determined; nor has Dr. Thomson succeeded, in any of the attempts he has made, to ascertain the proportions in which iridium unites with oxygen.

3. In order to obtain muriate of iridium, free from the other metal, the acid solution (2) was evaporated, and an imperfectly-crystallized mass obtained; but this, dried on blotting-paper, and again dissolved and evaporated, gave distinct octahedral crystals. The watery solution of these crystals had a deep red colour, inclining to orange. With infusion of galls no precipitation ensued; but the colour almost instantly disappeared. Muriate of tin, carbonate of soda, and prussiate of potassa, had the same effect. Pure ammonia precipitated the oxide, but retained a part, and acquired a purple colour. All the metals, except gold and platinum, precipitated iridium of a dark colour from the muriate which had lost its colour. From the composition of the muriate (or rather *chloride*) of iridium, Dr. Thomson determines the atomic weight of the chloride to be 66, and deducting from this the weight of an atom of chlorine, the atom of iridium will weigh 30. From analogy, the protoxide should consist of 30 iridium + 8 oxygen.

4. Iridium was obtained pure by heating the muriate, which expelled both the acid and the oxygen. It was of a white colour and perfectly infusible. But Mr. Children has since fused it by his immense galvanic battery into a metallic globule, which was white, very brilliant, and, though porous, had the high specific gravity of 18.68. (Phil. Trans. 1815, p. 370.) It did not combine with sulphur or arsenic. Lead united with it, but was separated by cupellation. Copper, silver, and gold, were severally found to unite with it, and it could not be separated from the two latter by cupellation with lead.—Its other properties remain to be examined.

Berzelius, in the analysis of native platiniferous sand, has



paid great attention to the properties and combinations of iridium. He finds that it is retained with so much force in the native alloy with osmium, that there is great difficulty in separating the two metals. He succeeded, however, by the fusion of the alloy with nitre, and by a series of processes, for which I must refer to his memoir. (Ann. de Ch. &c. Feb. 1829.)

Iridium combines with chlorine in four proportions, *viz.*, 1 atom with 2, 3, 4, and 6 atoms of chlorine, and each chloride forms double salts with the chlorides of potassium and sodium. There is great difficulty in forming any one of these per-chlorides, without, at the same time, giving rise to others. To each chloride there is a corresponding oxide, capable of forming peculiar salts with acids. These oxides are obtained by precipitating their equivalent chlorides with alkalis. There are also mixed oxides, which might lead to the opinion that iridium unites with oxygen in very numerous proportions. This circumstance accounts for the variety of colours in solutions of iridium, which exhibit all the hues of the rainbow.

Iridium combines with sulphur in the same proportions as with chlorine, all the chlorides being decomposable by sulphureted hydrogen, the hydrogen of which unites with the chlorine, and the sulphur with the metal.

II. 1. Osmium was procured in the state of an oxide, by simply distilling, at a gentle heat, the alkaline solution, obtained as already described (I. 1.) along with any acid. It was even found to escape, in part, when water was added to the dry alkaline mass remaining in the crucible; and was manifested by a pungent and peculiar smell, somewhat resembling that of chlorine gas, from which property its name has been derived. The watery solution of oxide of osmium is without colour, has a sweetish taste, and the strong smell already alluded to. Another mode of obtaining the oxide is by grinding together 3 parts of the ore of iridium and 1 of nitre, and introducing the mixture into a cold crucible. This is to be heated to a good red in an open fire, until the ingredients become pasty, when osmic fumes will be found to arise from it. The soluble parts are then to be dissolved in the smallest quantity of water adequate to the effect, and the liquid thus obtained is to be mixed in a retort with as much sulphuric acid, diluted with an equal weight of water, as is equivalent at least to the alkali in the nitre. By distilling rapidly into a clean receiver, for so long

a time as the osmic fumes continue to come over, the oxide will be collected in the form of a white crust on the sides of the receiver, and there melting it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. When the receiver is quite cold, the oxide will become solid and will crystallize. (Wollaston, *Phil. Trans.* 1829.)

M. Laugier having observed that nitro-muriatic acid, which has been employed to dissolve platinum, emits a strong odour of osmium, distilled the liquor, and saturated the product with quicklime; after which, by again distilling the liquid, he obtained a quantity of osmium sufficient to repay the trouble of the process. (89 *Ann. de Chim.* p. 191.)

A solution of oxide of osmium in water gives a stain to the skin that cannot be effaced. The most striking test of this oxide is an infusion of galls, which presently becomes of a purple colour, and afterwards changes to a deep vivid blue. With pure ammonia, the osmic solution becomes somewhat yellow; and slightly so with carbonate of soda. With alcohol, or still more quickly with ether, it acquires a dark colour, and, after some time, separates in the form of black films.

The odorous oxide of osmium, the precise composition of which is unknown, though it is suspected by Berzelius to be a deutoxide, gives up its oxygen to all the metals, excepting gold and platinum. When its solution in water is shaken with mercury, the solution loses its smell; and the metal, combining with the mercury, forms an amalgam. From this, much of the redundant mercury may be separated by squeezing it through leather, which retains the amalgam of a firmer consistence. The mercury being distilled off, the osmium remains in its metallic form, of a dark grey or blue colour, capable of assuming a polish under the burnisher. Its specific gravity is 10, in its most condensed, and 7 in its lightest, form. Exposed to heat with access of air, it evaporates with its usual smell; but, if oxidation be effectually prevented, it does not seem in any degree volatile. Being subjected to a strong white heat, in a cavity made in a piece of charcoal, it is not melted, nor does it undergo any change. With gold and silver it forms malleable alloys. These are easily dissolved in nitro-muriatic acid; and, by distillation, give the oxide of osmium with its usual properties. It is capable, also, of being alloyed with steel, as has already been stated in section 16.

The pure metallic osmium, not previously heated, is slowly soluble in ordinary nitric acid, but much more rapidly in the nitro-muriatic acid. If heated, it becomes less soluble. By heating it in a silver cup with alkali, it immediately combines with the alkali, and this compound gives, with water, a yellow solution, similar to that from which it had been procured. From this solution, acids expel the oxide of osmium, having its usual smell, and possessing the property of changing to a vivid blue the infusion of galls.

Osmium absorbs chlorine only when heated, and forms a compound which powerfully attracts moisture, and assumes a crystallized form. In the general mass, however, crystals of different colours, green, red, and yellow, are discoverable, which appear to be chlorides with different proportions of elements. These chlorides form compound salts with the chlorides of potassium and sodium, for an account of which the reader may consult the memoir of Berzelius already quoted. Equivalent to these, Berzelius has satisfied himself that there are 3 oxides constituted of 1 atom osmium with 1, 2, and 4 atoms of oxygen, and probably two others not yet insulated.

Besides the black powder from which osmium is obtained, Dr. Wollaston discovered a separate ore, or native alloy, of these two metals, mixed with the grains of crude platinum. The specific gravity of this ore is about 19.5, and therefore exceeds that of crude platinum itself, which is only 17.7. The grains are about the size of those of native platinum, but are considerably harder; are not at all malleable; and appear to consist of laminæ, possessing a peculiar lustre.

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## SECTION XXXIX.

### *Nickel.*

The principal source from which nickel is obtained is a substance called *speiss*, which remains at the bottom of the crucibles in which zaffre is prepared. (See Section on Cobalt.) *Speiss* is a compound of several metals, nickel constituting about half its weight, and the rest being made up of cobalt, copper, arsenic, and antimony, with a little sulphur and some earthy impurities. (Berthier, Ann. de Ch. et de Ph. xxiii. 94.)

A great variety of processes have been described by chemists for the extraction of nickel from its ore. Those who are interested in this subject may consult the papers of Richter in the 12th vol. of Nicholson's Journal; Robiquet in the 69th, and Tuppiti in the 78th vol. of the Annales de Chimie; Mill, in the Annals of Philosophy, N. S. iii. 201; Laugier, in Ann. de Ch. et de Ph. ix.; and Berthier, in the 25th and 33d vols. of the same work. I select the following process of Dr. Thomson, described in the Philosophical Mag. and Annals of Phil. for August, 1827, because, if equally effectual, it is least encumbered with a variety of operations.

Speiss, broken into powder, is to be dissolved in a mixture of sulphuric and nitric acids. The crystals obtained by evaporation are free from arsenic, iron, bismuth, and antimony, but are contaminated by a little cobalt and copper. The copper is to be precipitated from a watery solution of these crystals by a current of sulphureted hydrogen; and the oxide of nickel, when washed, but still moist, is to be exposed to chlorine gas, which dissolves the oxide of nickel, leaving that of cobalt untouched. The muriate of nickel is easily converted into sulphate, by the addition of a due proportion of sulphuric acid; and the sulphate, by one or more crystallizations, is obtained pure. From this salt, dissolved in water, carbonate of nickel is precipitated by carbonate of soda or potassa, and, after being welledulcorated, is to be dried and calcined.

To procure nickel in a metallic state from the pure oxide, Berthier mixes the latter with  $\frac{1}{9}$ th or  $\frac{1}{10}$ th its weight of finely-powdered charcoal, and with any convenient flux, and exposes it to an intense heat. Or he places the oxide in a cavity formed in a piece of charcoal, and submits this to heat, bedded in charcoal powder. If the metal, however, be wanted in a state of absolute purity, reduction by hydrogen gas is best adapted for the purpose, for this excludes contamination with charcoal. It may be forged while hot, after having been sprinkled with borax.

Nickel, when metallized, has the following characters:

Its colour is white, and intermediate between those of silver and tin. It admits of being finely polished, and has then a lustre between those of steel and platinum. When ignited, its colour changes to that of antique bronze, which is increased every time the metal is heated.

It is perfectly malleable, and may be forged when hot into

bars, and hammered into plates when cold. At  $54\frac{1}{2}^{\circ}$  Fahr., Tourte found its specific gravity 8.402, and, after being thoroughly hammered, 8.932. It is ductile, and may be drawn into very fine wire. It cannot easily be soldered, on account of the oxide which forms on its surface when heated. Its power of conducting heat is superior to that either of copper or zinc. It obeys the magnet, and is itself capable of becoming magnetic, properties which are retained even when it is alloyed with a little arsenic, and, as Lampadius has shown, with metals. In difficult fusibility by heat, it appears to equal manganese.

*Oxides of nickel.*—Nickel appears to be susceptible of two different states of oxidation. By long exposure to a red heat, with free access of air, it is converted into a dark brown oxide (dull olive, Berthier), which is still magnetic, and which loses, by ignition at a white heat in a charcoal crucible, 22.5 out of 100. (Berthier.) In oxygen gas, nickel burns vividly, and throws out sparks. When precipitated from its solution by alkalis, and moderately ignited, it becomes of an ash-grey colour with a slight tinge of blue or green. By farther ignition, it becomes blackish grey, and then consists, according to Richter, of 100 metal and 23.2 oxygen. Tuppiti, from 100 grains of nickel dissolved in nitric acid, precipitated by a fixed alkali, and calcined, obtained 127 grains of an ash-grey powder, which is to be considered as the *protoxide*. Hence it is composed of

Nickel . . . . .	78.8	. . . . . 100	. . . . . 1 atom =	29.5
Oxygen . . . . .	21.2	. . . . . 27	. . . . . 1 atom =	8.
	100.			37.5

This, however, differs considerably from the results obtained by Lassaigne, who found the oxide obtained by gently calcining nitrate of nickel, to consist of

Nickel . . . . .	83.34	. . . . . 100	. . . . . 1 atom =	40
Oxygen . . . . .	16.66	. . . . . 20	. . . . . 1 atom =	8
	100.			48

But Lassaigne stands alone in fixing so low a proportion of oxygen to the metal; and Berzelius and Berthier adopt the result of Rothoff, who found the oxide to consist of

Nickel . . . . .	78.71	. . . . . 100.	. . . . . 1 atom	29.6
Oxygen . . . . .	21.29	. . . . . 27.05	. . . . . 1 atom	8
	100.			37.6

Dr. Thomson again, from the composition of the sulphate, derives 26 for the atomic weight of nickel, and 34 for that of the protoxide. (First Prin. and Phil. Mag. Aug. 1827.) Mr. Phillips considers 29, and Mr Brande 30, as the equivalent of the metal, while Mr. Dalton deduces 29.71 (oxygen = 8) to be its atomic weight. (N. S. ii. 34.) With such a want of agreement, the subject must be considered as still open to further inquiry.

Thenard describes also a *peroxide of nickel*, obtained by passing a current of chlorine gas through water in which the hydrated protoxide is suspended. Its precise composition is unknown; but it has been stated by Rothoff to contain  $1\frac{1}{2}$  times as much oxygen as the protoxide, and it should, therefore, consist of 100 nickel + 40.075 oxygen. It has several analogies with oxide of manganese. Its colour is intensely black, and it evolves chlorine from muriatic acid. In a sufficiently high temperature, these oxides are reducible without addition; nor is nickel more tarnished by a strong heat than gold, silver, or platinum. It ranks, therefore, among the noble or perfect metals.

#### *Salts of Nickel.*

*Chloride.*—Nickel, when heated in *chlorine gas*, affords an olive-coloured compound, which is probably a *bi-chloride*. The muriate of nickel, when evaporated and strongly heated, affords brilliant yellow scales, which are probably the proto-chloride; but these compounds have not been sufficiently examined.

*Iodide of nickel* may be formed by precipitating any solution of nickel with hydriodate of potassa. It is insoluble, and of a green colour.

The *sulphuric* and *muriatic acids* have little action on nickel; but the former is enabled to dissolve it by additions of nitric acid, made in succession, till the solution is complete. Sulphate of nickel is a beautiful green salt in quadrangular prisms, which are not altered by exposure to the atmosphere. It has a sweetish and astringent taste; and is soluble in three times its weight of water at 69°. Sulphate of nickel forms sometimes rhombic prisms, and sometimes square prisms, but, on a careful analysis of these two varieties, Mr. Phillips could not find any difference amounting to an atomic disparity. (Ann. of Phil. N. S. vi. 437.) Dr. Thomson (First Princ. of Chem. ii. 133,) has analyzed this salt, with a view to ascertain the equivalent number of nickel, which he deduces to be  $3.35 = 26$ , oxygen being considered as 8. The sulphate he finds to consist of

	Atoms.	
Sulphuric acid . . . . .	29.2	or 1 = 40
Protoxide . . . . .	24.8	or 1 = 34
Water . . . . .	46.0	or 7 = 63
	100.	137

The appropriate solvents of nickel are the *nitric* and *nitro-muriatic* acids. The nitric solution has a beautiful grass-green colour, and on evaporation affords rhomboidal crystals, which have not been analyzed. Carbonate of potassa throws down an apple-green precipitate, which assumes a dark grey colour when heated. The fixed alkalis occasion a bulky greenish white precipitate, which is a hydrate or hydro-oxide of nickel, composed of 76 per cent. of the protoxide and 24 water.

When pure ammonia is added to nitrate of nickel, a precipitate is formed, resembling that which is separated by ammonia from a solution of copper, but not of so deep a hue. This colour changes, in an hour or two, to an amethyst red, and to a violet; which colours are converted to apple-green by an acid, and again to blue and violet by ammonia. If the precipitate retain its blue colour, the presence of copper is indicated. (See Richter in Nicholson's Journal, xii.) This precipitate, which is a hydrate, is redissolved by an excess of ammonia; and by this property the oxide of nickel may be separated, in analysis, from those of almost all other metals.

From the solutions of nickel, *ferro-cyanate of potassa* throws down a sea-green precipitate. According to Bergman, 250 parts of this contain 100 of metallic nickel. This statement, however, differs considerably from Klaproth's, according to whom 100 grains of nickel, after solution in sulphuric acid, give a precipitate by prussiate of potassa, which, after being ignited, weighs 300 grains.

Tincture of galls produces no change in solutions of nickel.

Arseniate of potassa precipitates from the nitrate a pale green arseniate of nickel; soluble, according to Berzelius (Ann. de Chim. et de Phys. xvii. 220), in pure ammonia. From this solution, potassa throws down a compound of oxide of nickel with potassa, and the acid of arsenic remains united with the alkali.

The solutions of nickel do not deposit the metal either on

polished iron or zinc. (See Klaproth's Analytical Essays, i. 433.) All that takes place by the action of zinc, is the separation of a mud-coloured precipitate, consisting, for the most part, of arsenic and iron, with which nickel generally abounds. Hence the green colour of the solutions of nickel is greatly improved by the action of zinc.

*Sulphurets of nickel.*—Solutions of all the salts of nickel are decomposed by alkaline hydro-sulphurets, with which they form black precipitates; but sulphureted hydrogen has no effect on them. Nickel may, however, be combined directly with sulphur by fusion, and forms a grey compound with a metallic lustre. The proto-sulphuret contains, according to Mr. Davy's experiments, 34 per cent. of sulphur; and the bi-sulphuret, which may be formed by heating the protoxide with sulphur, is stated, by the same chemist, to contain 43.5 per cent. of sulphur. In the proto-sulphuret, therefore, 100 of metal are united with 51.51 sulphur, which, divided by 2, is not very remote from the oxygen stated by Tuppiti to constitute the protoxide; while in the bi-sulphuret, 100 of metal are combined with 77 of sulphur, which is pretty exactly a multiple of 51.51 by 1.5.

Berthier obtains sulphuret of nickel by fusing the arseniuret with carbonate of soda and sulphur, but the product is mixed with sulphurets of arsenic and sodium, both of which may be removed by water. The sulphuret, after fusion, resembles exactly iron pyrites. Its sp. gr. is 5.76; it is not attacked by sulphuric or muriatic acid; but nitric acid dissolves it, when heated. Like the olive compound it is a bi-sulphuret. (Ann. de Ch. et de Ph. xxxiii. 57.)

*Carburet.*—Nickel is susceptible of uniting with carbon, and is apt indeed to form this union, when reduced from its salts by carbonaceous matter. According to Mr. Ross, it composes a substance resembling iodine or micaceous iron ore. (Ann. of Phil. N. S. ii. 62, 149, and iii. 201.)

Nickel may be alloyed with most of the metals, but the compounds have no particularly interesting qualities. An alloy of iron and nickel has been found in all the meteoric stones that have hitherto been analyzed, however remote from each other the parts of the world in which they have fallen. In these, it forms from  $1\frac{1}{2}$  to 17 per cent. of their weight. It enters, also, into the composition of the large masses of native iron discovered in Siberia and in South America; and was found by Mr. Brande



to the extent of 3 per cent. in native iron brought from the Arctic regions.

To detect, in a general way, the presence of nickel in iron, Dr. Wollaston recommends that a small quantity (which need not exceed  $\frac{1}{100}$  of a grain) should be filed from the specimen; dissolved in a drop of nitric acid; and evaporated to dryness. A drop or two of pure liquid ammonia, added to the dry mass and gently warmed, dissolves any nickel that may be present. The transparent part of the fluid is then to be led, by the end of a glass rod, to a small distance from the precipitated oxide of iron; and the addition of a drop of triple prussiate of potassa detects the presence of nickel by the appearance of a milky cloud, which is not discernible in the solution of a similar quantity of common wrought iron treated in the same manner. The method of ascertaining with precision the quantity of nickel in its alloy with iron, employed by the same philosopher, will be described in the chapter on mineral analysis.

## CHAPTER X.

## VEGETABLE SUBSTANCES.

VEGETABLE substances, though distinguished from each other by peculiar characters, present several circumstances of agrément as to chemical properties. Oxygen, hydrogen, and carbon, are their principal ingredients, with which a certain proportion of nitrogen is sometimes united; and variations in the proportions, and mode of combination, of these elements, occasion the great diversity which subsists among the products of the vegetable kingdom. They are all susceptible of decomposition by heat alone; but we cannot always, as in bodies of the mineral kingdom, proceed from a knowledge of their components to the actual formation of the substances themselves. It is not probable, indeed, that we shall ever attain the power of imitating nature in these operations. For, in the functions of a living plant, a directing vital principle appears to be concerned, peculiar to animated bodies, and superior to, and differing from, the cause which has been termed chemical affinity.

The productions, of which I am about to offer the chemical history, may be regarded as the *immediate* or *proximate principles* of vegetables; for we may presume, generally speaking, that they exist in the living plant in a state identical with that under which chemical processes exhibit them. It is not so when we proceed to the *ultimate* analysis of vegetables; for, in that case, we obtain compounds, which formed no part of the vegetable structure, and which result from an entirely new arrangement of the elements composing it. Acetic and carbonic acids, for example, are obtained by the destructive distillation of several vegetable substances, in which neither of those acids existed ready formed, but only their elements.

The destructive distillation of vegetables, or the subjecting them to the action of heat in close vessels, with a view to collect both the condensible and aëriform products, was, until within a few years past, the only method employed to determine the proportion of their ultimate elements; but more refined and perfect modes of analysis were introduced by Gay Lussac and

Thenard, which have afforded results much more deserving of confidence. (*Recherches Phys.-Chim.* ii.) The object of these improved processes, which are equally applicable to vegetable and animal substances, is to convert the whole of the carbon into carbonic acid, and the whole of the hydrogen into water, by means of some compound containing oxygen in so loose a state of union, as to give it up to those elements at the temperature of ignition. The following illustrations are intended to explain the rationale of the process.

*Ultimate Analysis of Organic Substances.*

1. If we have charcoal only, mixed with incombustible matter, and wish to determine its quantity, all that is necessary is to expose a known weight of the substance under examination, in a state of perfect mixture with a fit oxide (peroxide of copper, for instance) to a red heat, and to collect the carbonic acid. From the volume of this gas, its weight may be easily calculated; and of this weight six parts in 22 are pure carbon.

2. Let us next suppose that we are operating on a compound of charcoal with hydrogen. This, if solid, must be mixed with an excess of the oxide employed, and the carbonic acid collected as before. Calculating, by the same method, the quantity of charcoal which it contains, we obtain the weight of one element of our unknown compound; and this, deducted from the weight which was submitted to experiment, gives the weight of the remaining element, hydrogen. To attain still greater certainty, the water, which is formed, may be actually collected, by a proper addition to the apparatus, either at the same operation with the carbonic acid, or at another, performed expressly for the purpose. Of this water, one part in nine is hydrogen. The carbon, calculated from the carbonic acid, and the hydrogen from the water, should together make up precisely the weight of the compound on which we have operated.

3. A third case may be supposed, in which carbon and hydrogen are united with oxygen, but yet not with enough to convert them entirely, at a high temperature, into carbonic acid and water. In this case, the first steps of the operation are the same as before. But on summing up the results, the weight of the carbon and hydrogen, discovered in the products, will be found to fall short of the weight of the substance submitted

to experiment. If no other product has been formed, beside water and carbonic acid, the deficiency may safely be placed to the account of oxygen. For example, if from 10 grains of a supposed compound of hydrogen and carbon we obtain, by ignition with an oxide, 22 grains of carbonic acid and 9 grains of water, these are equivalent to 6 grains of carbon and 1 of hydrogen: but  $6 + 1 = 7$  leave a deficiency of 3 grains, which are probably oxygen. To verify this conclusion, if at all doubtful, it may be proper to examine what quantity of oxygen has been lost by the oxide employed to effect decomposition; and if this fall short of the oxygen contained in the carbonic acid, and in the water, then the quantity required to make up the sum must have previously existed in the subject of analysis. For instance, in the supposed case, we find 16 grains of oxygen in the carbonic acid and 8 in the water obtained, together 24; but if the oxide can be shown by experiment to have lost only 21 grains, we may safely conclude that 3 grains pre-existed in the compound.

4. In a few vegetable substances, and in almost all animal ones, beside carbon, hydrogen, and oxygen, azote or nitrogen exists as a component, and its quantity requires to be determined. With a proper attention to the details of the process, this fourth element may be obtained in the state of a gas, which remains after absorbing the carbonic acid by solution of potassa, and the oxygen (if any) by a fit agent. From the volume of the gas, its absolute weight may easily be calculated. (See the subsequent section on the analysis of mixed Gases.)

Such is the process employed for the decomposition of vegetable and animal substances, divested, for the purpose of rendering its objects and results more intelligible, of all details. These details, however, are of the greatest importance in practice, and will be presently stated at length. It may be proper here to remark, that all the analyses which have been thus performed, and which are worthy of confidence, conspire to prove that the elements of organized, like those of inorganic matter, are united in definite proportions; and farther, that the law of simple multiples holds strictly with respect to the elements of organic bodies. We may derive, therefore, as has been well observed by Dr. Prout, the most valuable assistance in our researches into organic compounds, from the use of Dr. Wollaston's scale of chemical

equivalents. (Ann. of Phil. iv. 270.) To fit it for this purpose, he recommends that it be extended a little, by pasting two slips of drawing-paper on its edges, of such a breadth as just to lap over and cover the margins, containing the names of the chemical substances generally marked upon it, and to coincide with the graduated edges of the slide. On these slips of paper are to be marked the multiples of an atom of oxygen, hydrogen, and carbon, from one to ten; and of azote from one to four or five, or more. Thus prepared, it will be easily applied, by all who are acquainted with the principle of the instrument, to the purposes of facilitating and verifying analyses, the results of which can be rigorously correct, only when they agree with some of the proportional numbers, marked upon the scale. For example, an analysis showing 48 parts of oxygen, 6 of hydrogen, and 36 of carbon in a vegetable compound, or quantities proportional to these, agrees with six atoms of each of those elements. But such an alteration of any of those numbers as would indicate the fraction of an atom (the reduction of the carbon, for instance, to 34) would be inconsistent with the law of simple multiples, and would suggest the necessity of a fresh appeal to experiment.

The agent, first employed by Gay Lussac and Thenard in the combustion of organic substances, was the *chlorate of potassa*, applied by means of an ingenious apparatus, which is described in the second volume of their *Recherches Physico-chimiques*, and also in Mr. Children's translation of Thenard on Chemical Analysis. For chlorate of potassa, Gay Lussac, in 1816, substituted the *peroxide of copper*, which, being found to afford more accurate results, with a less complicated apparatus, and fewer difficulties of manipulation, is now generally preferred, especially in the analysis of animal compounds. Peroxide of copper may be prepared for this purpose by calcining on a muffle the scales or filings of that metal, pulverizing and again igniting them on the muffle, and repeating these operations till the metal is completely peroxidized. For scales or filings of copper, the residuum of the distillation of binacetate of copper may be substituted; or we may obtain the peroxide, by exposing the nitrate to a low red heat. Mr. Cooper prefers the oxide prepared from the binacetate, and advises that it should be sifted, first through a fine wire sieve, and then through a lawn one; the fine dust which passes the latter being rejected as not adapted to the purpose.

Several variations in the method of proceeding have been recommended by different experimenters. The tube, for containing the mixture of the oxide and body to be analyzed, is by some preferred of copper, by others of crown or green bottle-glass; and the heat has been applied, either by encompassing the tube with burning charcoal, or with the flame of a spirit lamp. Glass tubes of about 1-3d of an inch bore, or of a diameter adapted to the quantities operated upon, seem, on the whole, to be preferable to metallic ones; and the heat of a spirit lamp, used in the most improved manner, appears to me adequate to effect a complete decomposition of most vegetable and animal compounds.

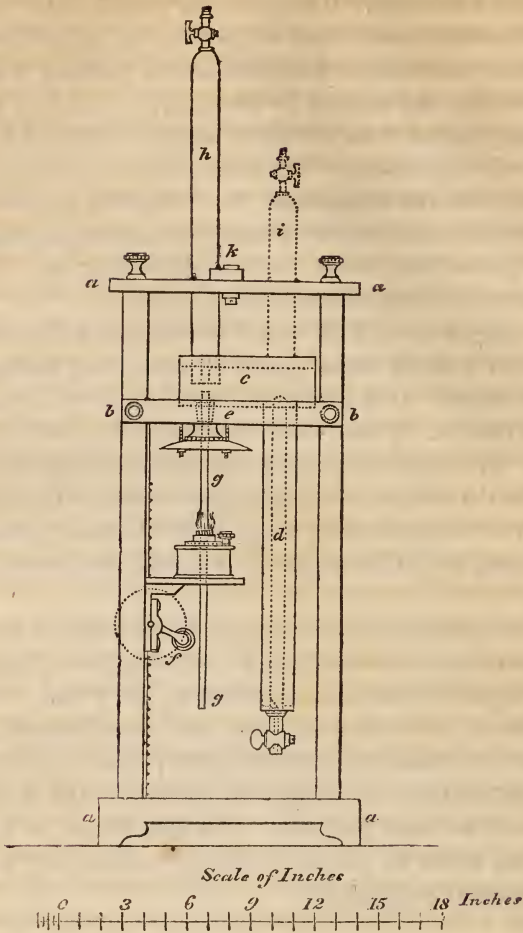
If the substance be a solid, from 3 to 5 grains are to be carefully dried, which is best done by placing it in fine powder under an exhausted receiver along with sulphuric acid. An apparatus for drying substances *in vacuo*, at a temperature of 212° Fahr., is described by Dr. Prout in Ann. of Phil. vi. 272. To those, who have not an air pump, Mr. Cooper recommends a wide-mouthed vial furnished with an accurately-ground stopper, and another smaller vial that will easily go into it, and will allow the stopper to be fixed in its place. A little tallow is to be applied to the stopper, to ensure its fitting accurately. Strew on the bottom of the larger vial a quantity of dry chloride of calcium; put into the smaller vial the substance intended to be dried; and place this in the larger vial standing on the chloride; moisten a small bit of paper with alcohol, and put it into the larger vial, but not within the smaller one. When thus arranged, set fire to the moistened paper, and when it has burned a second or two, put the stopper into its place. A sufficiently good vacuum is in this way formed, and the process of desiccation goes on rapidly.

The materials, when dry, are to be triturated in a glass or porphyry mortar, first by themselves, and then with 120 or 200 grains of the peroxide of copper, added by degrees, so that the substance and the oxide may be thoroughly incorporated. This mixture must be transferred, with the most scrupulous care to avoid loss, into the glass tube, and a little more of the peroxide must be triturated in the mortar, to collect any remains of the substance under analysis, and then added to the contents of the tube. Over these, 20 or 30 grains of the peroxide may be placed; and the remainder of the tube may be filled with per-

fectly dry amianthus. The peroxide should either have been recently cooled from a state of ignition, or, as advised by Dr. Ure, have been suffered to imbibe all the moisture it is capable of absorbing, and assayed for the quantity, which in that case, must be deducted from the loss of weight, sustained by the peroxide in the experiment. The whole, however, of what has been absorbed from the atmosphere, Dr. Prout finds is not water, but that air also is condensed by the recent peroxide, and constitutes  $\frac{1}{3}$ rd or  $\frac{1}{4}$ th of the increase of weight, which, on 100 grains, amounts to between .02 and .05 of a grain.

To operate on a fluid, Dr. Ure encloses it in a small bulb capable of holding three grains of water, and having a small pointed orifice. It is easy to fill such a bulb by first expelling the air from it by heat, and then immersing its orifice in the liquid. The bulb thus filled, and carefully weighed, is to be placed at the bottom of the tube, and covered with the requisite quantity of the peroxide of copper. In all cases, the tube, with its contents, should be accurately weighed, and its weight registered.

For the purpose of applying heat to the tube, and obtaining the gaseous products with only a small quantity of mercury, an useful apparatus has been contrived by Dr. Prout. Of this I am induced, by having witnessed its successful application in his hands, to retain the annexed sketch; more especially as no other representation of it has been published, and as Dr. Prout still uses it for some purposes. For most others, he prefers an apparatus, which he has more recently constructed, and which will presently be described.



Two square upright pillars are morticed into a square tray (*a* at the bottom of the figure) about  $\frac{3}{4}$ ths of an inch deep, and are fixed at the top by brass screws into a flat shelf of wood, 3 in. broad at each end, and 5 in the middle, in which is an oval slit or hole  $4\frac{1}{2}$  inches long and  $1\frac{1}{4}$  wide, distant  $1\frac{3}{4}$  inches from the right hand extremity of the shelf. Below this is another shelf, *b b*, which is moveable by a rack and pinion worked by a small handle, shown at *f*. Into a shallow cavity in this shelf is fixed a cistern of copper covered with hard varnish (cast iron would be better) and having a deep cylindrical cavity or well at *d*. This, to economize mercury, may occasionally be filled with



a plug of wood or cast iron. The cistern may be of any convenient dimensions, as  $5\frac{1}{4}$  long by  $1\frac{1}{2}$  wide, and in its bottom, an opening is required about  $\frac{5}{8}$ ths of an inch diameter for admitting the glass tube *g g*, which is secured in its place by a perforated cork, and is passed also through the axis of a brass spirit lamp, which, as well as the wick, has a circular hole for the purpose. The lamp is placed on a small shelf, perforated also, and moveable by the rack and pinion. A small mirror of tin, with the concave side downwards, is screwed to the bottom of the cistern, to guard the cork from being burned by the heat of the lamp. At *k* is a turning button with a semicircular notch for securing in an upright position the jar *h* which should be capable of containing 7 or 8 cubical inches.

The tube *g g* being fixed in its place, and the jar *h* filled with and inverted in mercury, the spirit lamp is set as high as its carriage will permit, and lighted. The part of the tube, which is surrounded by the burning wick, soon becomes red-hot, and gas is evolved. When it ceases to issue, the lamp may be gradually lowered, so as to heat successively the whole of the tube, and then moved upwards to the top. When this has been skilfully performed, the whole of the substance under analysis will be found to have been decomposed; but to ensure accuracy, its contents may be taken out, triturated in a mortar, and subjected to a repetition of the same operation. The gases obtained must be exposed to the action of liquid potassa, which will absorb the carbonic acid. In measuring the residue, it will be necessary to equalise the level of the mercury within and without the receiver, by immersing it in the well *d*. The residuary gas will probably be nitrogen only, but it may be assayed for oxygen by nitrous gas, as described vol. i. p. 313. The gases must of course be either measured at a mean of the barometer or thermometer, or the proper corrections made for deviations from these standards, as well as for aqueous vapour, by the rules already given vol. i. p. 25, &c.

To collect the water, a separate operation on another portion of the substance is necessary. When this is done, the mercurial cistern may be removed; and such a condensing apparatus substituted, as will be obvious to persons conversant with chemical processes. This is the method followed by Berzelius, but Dr. Prout prefers estimating the quantity by the loss of weight sustained by the tube after the combustion, at least in the majority of cases.

By the original apparatus of Dr. Prout, a part only of the tube and its contents can be heated at once. This is of little consequence when solid bodies are acted upon; but in the decomposition of liquids, or of solids yielding liquid products, it is desirable to ignite a greater length of the tube at a time. To effect this, Mr. Cooper of Lambeth, employs a lamp, which appears to me very well adapted to the purpose, and which he has described, and represented by an engraving, in a paper printed in the 41st vol. of *Trans. of the Society of Arts*, and copied into the *Ann. of Phil. N.S.* vii. 170, and the *Quart. Journ.* xvii. 232. It is figured also in Mr. Faraday's *Chemical Manipulation*, page 305. The lamp is of tin, in the shape of a parallelopipedon, 8 inches long and  $1\frac{1}{4}$  square, with 10 flat wick-holders fixed at equal distances and at a small angle with its upper surface, each wick-holder being half an inch broad and  $\frac{3}{8}$ ths of an inch high. Of these lamps two are necessary, and they are set on a small tin tray which is raised on four feet, and has a longitudinal slit in the middle  $7\frac{3}{4}$  inches long and  $\frac{3}{8}$ ths of an inch wide. On this tray the lamps are placed with their wicks opposite to, and sloping towards, each other; and the tube, containing the mixture to be decomposed, which is of green glass, sealed hermetically at one end, 14 or 15 inches long, and about the diameter of a small quill, is placed horizontally over the wicks at a suitable distance, one end of the tube having been first bent by a lamp into such a form, that its open extremity can be placed under a jar inverted in mercury. Or instead of operating with a tube of one piece, which renders it necessary to bend the open extremity, a shorter piece, properly bent, may be attached to the tube containing the materials, by a small collar of elastic gum. This removes the liability to accident from stiffness in the end of the tube, and the containing tube, being straight, may be used repeatedly. The tube is defended from too sudden or excessive heat, by being wrapped spirally round with copper-foil. The wicks nearest to the mercurial trough may be first lighted, and the remainder in succession as the former finish their action. It is easy, as Mr. Cooper was so good as to show me, by altering the distance of the flames from the tube, and of the lamps from each other, to modify the application of the heat as the circumstances of the experiment may require, and if it be desirable to kindle only particular wicks, this may be effected by interposing slips of tin between them and

those which are next to them. The alcohol, to prevent its too rapid combustion, Mr. Cooper dilutes with water to the sp. gr. of about .860. In certain cases, it appears to me that it may be advantageous to combine the apparatus of Mr. Cooper with the mercurial trough of Dr. Prout, as was done by Mr. Faraday in the analysis of sulpho-naphthalic acid.

Long and extensive practice in vegetable analysis has recently suggested to Dr. Prout, what he considers important improvements in the construction and use of apparatus adapted to these refined experiments. In the Philosophical Transactions for 1827, he has described, and represented by a plate, the apparatus, which he is now in the habit of employing, in cases to which the vertical one, depicted in page 196, is less adapted. This paper, illustrated by a plate, without which the description would be unintelligible, is copied into the Ann. of Phil. for January and February 1828. To the general reader, it may be sufficient to state that Dr. Prout now employs, for containing the subject of analysis, a tube of bottle glass about 1-5th of an inch diameter inside, and moderately stout, which is placed in a horizontal position, and heated by a lamp furnished with a row of 24 small wicks. Each end of the tube is connected, by a right-angled tube of iron and vertical stop-cock, with a glass tube which stands upright and is accurately graduated into hundredths of a cubic inch; and this tube at its lower end is cemented into an iron tube, bent into a semicircular form, into the opposite opening of which another upright glass tube is fixed by cement, so that the two glass tubes, thus connected, form an inverted syphon. Both these syphons are furnished at their open ends with a funnel for pouring in mercury, and at the lower part of their bends with a cock for drawing it off. The syphons serve the purpose of small gasometers, and enable the operator to pass oxygen gas at pleasure over the subject of analysis; to measure, with the utmost nicety, the change, if any, in the volume of the oxygen gas; and to take out a portion for examination. The method generally found to succeed best, is to mix the substance with peroxide of copper, to heat the mixture by itself in the tube in the first place; and afterwards to send oxygen gas through the ignited and partially reduced oxide, by means of which it again becomes peroxidized, and any portion of the substance, that had escaped combustion, is thus completely burned.

When nitrogen is present in the body to be analyzed, it is apt to become oxidized at high temperatures by the oxide of copper. To obviate this as much as possible, Mr. Cooper has sometimes used protoxide instead of peroxide of copper; and though even this, under some circumstances, imparts oxygen to the nitrogen, yet it is less apt to do so. The protoxide is prepared by fusing the peroxide with copper filings in excess, and pulverizing and sifting the mass when cold.

Another source of error, pointed out by Bischoff, is that part of the carbon, sometimes amounting to 1-12th of the whole, escapes in the state of carbonic oxide, which, not being absorbed by potassa, mingles with the residuary nitrogen and increases its volume, while the carbon, by the diminished production of carbonic acid, is underrated. If there be reason at any time to suspect that this has happened, it will be easy to determine how much carbon exists in the residuary gas, by mixing a portion of it with about half a volume of hydrogen and the same quantity of oxygen, and detonating the mixture by an electric spark. By this combustion, the carbonic oxide will be converted into carbonic acid. (*Ann. of Phil. N. S.* viii. 308.)

Those, who prefer employing the heat of charcoal, may consult the description of an apparatus, contrived by Dr. Ure for that purpose, in the *Phil. Trans.* for 1822, p. 460. From experience, however, of the effects of the heat obtained by the combustion of alcohol, the spirit lamp appears to me fully sufficient, with the advantage of being much more cleanly and manageable than a charcoal furnace.

The whole of the operations, connected with the ultimate analysis of vegetable and animal substances, require great skill and experience, in this particular kind of research; and without much practice, persons, who may be well versed in the general processes of chemistry, must not expect to obtain accurate results. A single experiment should never be depended upon; but the analysis of each substance should be several times repeated, and a mean taken of those which do not present any very striking disagreement, excluding those results which vary so much from the average, as to lead to a suspicion of some failure in the manipulations.

It may sometimes perhaps, on a first view, excite suspicion of the accuracy of the results of ultimate analysis, when we remark the very near coincidence not only with respect to the

*kind*, but even to the *proportions* which have been thus deduced, of the elements of substances, differing essentially as to their chemical and sensible properties. In the instances of gum, sugar, and starch, the differences of composition, discovered by the experiments of Gay Lussac and Thenard, are so extremely small, as not to indicate any difference either of the kind or the number of elementary atoms. Acetic and succinic acids, also, afford on analysis the same elements in the same proportions. The results, however, are not, in this or similar cases, to be pronounced, for that reason only, to be inaccurate; for it is probable that in vegetable substances it is not only the *number* and *kind* of the respective atoms, but the *mode of their arrangement*, which occasions their distinctive characters. This view of the subject is confirmed, when we observe the important changes in the properties of vegetable substances, and the convertibility of those, which appear so nearly allied into each other, by slight causes, such as trifling alterations of temperature, or weak chemical agents. In cases of this sort, Dr. Prout has remarked, the only points of difference that can be traced, are the presence of a little more or less water, or the intimate mixture of a minute portion of some foreign fixed body. There is no term, he adds, at present employed, which expresses this condition of bodies; and, to avoid circumlocution, he adopts provisionally the term *merorganized* (*μέρος pars vel partim*), meaning to imply by it, that bodies on passing into this state become *partly, or to a certain extent*, organized. Thus he considers starch as *merorganized* sugar, having the same essential constitution, but differing from sugar by containing minute portions of other matters, which probably prevent its constituent particles from arranging themselves in the crystalline form, and thus cause it to assume totally different sensible properties. (Phil. Trans. 1827. p. 374.)

From a review of their experiments on the analysis of vegetable substances, Gay Lussac and Thenard deduced the following general conclusions:

I. A vegetable substance is always acid, when the oxygen, which it contains, is to the hydrogen in a proportion greater than is necessary to compose water. In this case, Dr. Prout observes, the substance increases the volume of a quantity of oxygen in which it is burned.

II. A vegetable substance is always resinous, or oily, or

alcoholic, &c., when the oxygen, contained in it, is to the hydrogen in a less proportion than in water. Substances of this kind, when burned in oxygen gas, diminish its volume.

III. A vegetable substance is neither acid nor resinous, but in a state analogous to sugar, gum, starch, lignin, &c., whenever oxygen and hydrogen enter into its composition in the same proportions as in water. In this case, combustion in oxygen neither increases nor diminishes the volume of the gas.

Without supposing, then, that oxygen and hydrogen actually exist, as water, in vegetables, we may, for the sake of illustration, consider vegetable acids, as constituted of carbon, water, and oxygen;—the resins, alcohol, ether, &c., as composed of carbon, water, and hydrogen;—and bodies of the third class, as composed of carbon and water only. Some exceptions to the generality of these principles have been pointed out by Saussure, and by Mr. Daniell. (*Ann. of Phil.* vi. 431. *Quart. Journ.* vi. 326.) But though the conclusions are true only to a certain extent, Dr. Prout considers them as sufficiently general to form the basis of a convenient arrangement of vegetable substances.

The products of the vegetable economy are either situated in particular organs or vessels, or are distributed throughout the whole plant. Sometimes they reside in the root or stalk; at others in the bark or leaves; at others they are peculiar to the fruit, the flowers, the seeds, or even to particular parts of these organs. When thus insulated, they may readily be procured in a separate state; and, in several instances, nothing more is required than the labour of collecting them. Thus gum exudes from some trees, and manna issues from the branches of others. Sometimes, however, we are presented with a variety of substances mingled together, and requiring separation by processes which are sufficiently simple, and which consist in repose, filtration, pressure, washing, distillation at a gentle heat, solution by water and alcohol, and similar operations, that do not alter the nature of the bodies submitted to them. Robinet has, also, found powerful agents in the solutions of neutral salts, each of which has its peculiar action on the proximate principles of vegetables. (*Ann. de Ch. et de Ph.* xxx. 210.)

The number of principles, which have thus been extracted from vegetables, has of late years been greatly enlarged, and amounts at present to upwards of forty. Of these, the greater

part are certainly entitled, by a train of properties sufficiently characteristic, to rank as distinct compounds. But others seem to be so nearly allied to substances with which we have long been acquainted, that it can serve no useful purpose to assign to them a different place in the system. The unnecessary multiplication, indeed, of vegetable principles contributes rather to retard than to advance the progress of this difficult part of chemistry; and it is only in cases of decided and unequivocal differences of qualities, that we should proceed to the establishment of new species.

Before dismissing the subject of the general properties of vegetable matter, it is proper to notice the interesting memoir of M. Chevreul "on the simultaneous Action of gaseous Oxygen and Alkalis on organic Substances." Of this essay, I have seen only a brief outline in the Quarterly Journal of Science, vol. 20, p. 388. It appears that many vegetable substances, (hematine, the colouring principle of Brazil-wood, cochineal, gallic acid, &c.) unite with alkaline liquids, and form compounds, which retain their properties so long as the liquids are carefully excluded from oxygen. But when brought into contact with atmospheric air, or still more rapidly with oxygen gas, the vegetable matter is decomposed, oxygen is absorbed, and carbonic acid is produced. This subject is well worthy of further investigation.

#### *Incineration of Vegetables, and Analysis of their Ashes.*

By the ultimate decomposition of vegetable substances, effected in the manner which has just been described, we can determine the proportions of oxygen, hydrogen, carbon, and azote with great accuracy. But there are other ingredients of vegetables, which form so small a relative quantity of their weight, that it is necessary, in order to discriminate them, to operate on large quantities. Of this class are the neutral salts, alkalis, earths, acids, and metallic oxides, which are discoverable, in greater or less number, in the ashes of all plants. They had not escaped the notice of the older chemists, some of whom have given their proportions in a tabular form, but though often correct as to the quantities of ashes, obtained by burning given weights of vegetables, yet the accurate separation of the different saline and oxidized matters from each other, requires all the refinements of modern analysis. Saussure resumed this

inquiry, and in his *Recherches sur la Végétation*, published in 1804, has given the results of his labours in this branch of vegetable analysis; and Berthier, in the *Ann. de Ch. et de Ph.* for July 1826, has published an excellent memoir on the analysis of the ashes of different kinds of wood. It is only the general results of these inquiries that I can notice, consistently with the limits of this work.

The ashes of vegetables are best obtained for experimental purposes, by a slow and smothered combustion, effected by burning them in a stove or small furnace, so constructed as to allow the quantity of air that is admitted to be well regulated. Too rapid a current of air not only carries away the lighter part of the ashes, but, by exciting excessive heat, vitrifies those that remain. The ashes, properly prepared, are resolved, by the action of warm water, into soluble and insoluble matter. The soluble are alkaline salts, having for their bases potassa and soda, united with carbonic, sulphuric, muriatic, and sometimes a trace of phosphoric acids, and almost always with silica. The insoluble residue consists of lime and magnesia, united with carbonic and phosphoric acids, of silica, and of oxides of iron and manganese. When the heat has been intense, lime is found in a free state, and a small proportion of unburnt carbonaceous matter is always discoverable. If after igniting the ashes on a muffle, or otherwise freely exposing them to the air, they continue to have a greyish colour, this generally arises from the presence of oxide of manganese. It is remarkable that though all vegetables grow in soils containing abundance of clay, yet alumina is not discoverable in their ashes. Silica is seldom abundant in the ashes of wood, but is found in considerable quantity in the ashes of graminiferous plants.

The proportion of ashes from different vegetables, and from different parts of the same plant, has a considerable range. Woods afford from 1.5 to + 3 per cent, rarely 5; but the ashes of bark rise even to 6 per cent.; of the straw of wheat 4.3, and of ripe grain 3.3. The soluble and insoluble ingredients of the ashes are present also in variable proportions, the soluble ranging from 12 to 30 per cent., and the insoluble from 70 to 88 per cent., of the whole incinerated product. The soluble salts are composed of potassa and soda united with carbonic, sulphuric, and muriatic acids, with silica, and with water, in ever-varying proportions. Woods in general furnished, in Berthier's



experiments, only about  $\frac{1}{30}$ th of their weight of alkaline salts; but the stalks and roots of potatoes gave  $\frac{1}{30}$ th, and in the latter case the proportions were, in 10 parts 2 of carbonate, 5 of sulphate, and 3 of muriate of potassa. The insoluble residue comprehends carbonic acid in combination with lime and magnesia; phosphoric acid united with lime as a sub-phosphate, and probably with potassa; and oxide of manganese.

Woods of the same species, growing in situations remote from each other, differed remarkably in the composition of their ashes; a sufficient proof of the influence of soil. Among woods growing on the same spot, there was found to be an analogous composition of their ashes, provided they belonged to the same genus; but woods of different genera, though growing contiguously, gave ashes differently composed. The ashes were found also to be considerably modified, when procured from different parts of the same tree. Thus, the large branches of the oak gave ashes which afforded 15 per cent. of alkaline salts, while ashes from the bark of the same tree gave only 5 per cent. of those salts, and contained, moreover, 7 per cent. of oxide of manganese. The ashes of wheat-straw consist almost wholly of silicate of potassa, while the grain contains only phosphate of lime. These facts, as Berthier observes, show that out of the substances presented by the soil to vegetables, such only are chosen by them as best suit their organization and their wants.

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## SECTION I.

### *Vegetable Extract, or Extractive.*

The term Vegetable Extract is not to be understood in the sense which is generally annexed to it, especially in pharmacy, as comprehending all those parts of vegetables which may be dissolved in water, and obtained in a solid form by evaporating the solution; but has been limited to a distinct and peculiar substance. The existence, however, of any vegetable principle, entitled to that name, has been doubted by Postock, Braconnot, and other writers who have devoted their attention to vegetable chemistry. Braconnot, with whom Berzelius concurs, has shown that all the properties characteristic of *extract*, belong also to *tannin*, insomuch that extract is probably *modified tan*. (Ann.

de Ch. et de Ph. xxvii. 335.) These properties are the following: It is soluble in cold water, but more abundantly in hot, and the hot solution becomes turbid on cooling. By gentle evaporation, a semi-transparent mass is obtained, but an opaque one at higher temperatures. By repeated solutions and evaporations, it becomes dark-coloured, and loses its solubility. It is soluble in weak alcohol, but not in pure alcohol or in ethers, and is precipitated by chlorine from the watery solution as a dark yellow powder, insoluble in water at any temperature, but soluble in alcohol. It has a great affinity for alumina, and by means of that basis may be applied to give a fawn colour to cloth.

The extract, obtained by decoction and evaporation from saffron, formerly taken as the best example of the extractive principle, has been the subject of a series of experiments by Bouillon la Grange and Vogel; who, considering it as a distinct principle, have given it the name of *Polychroite*, on account of the many different colours which it is capable of assuming. (80 Ann. de Ch. 188.) Thus its natural colour is yellow; and its aqueous solution is deprived of colour by exposure to the sun's rays. Sulphuric acid dropped into the aqueous solution causes a deep indigo-blue colour; nitric acid a green one; and chlorine renders it colourless. It may, however, be doubted whether these changes are not produced in some substance accompanying the extract, rather than in the extractive matter itself.

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## SECTION II.

### *Mucilage, or Gum.*

This substance, termed mucilage when fluid, is, in a solid state, generally known by the name of gum. Gum arabic may be taken as an example. It exudes through cracks in the bark of the trunk and branches of a tree, a species of *acacia*, and hardens spontaneously into yellowish drops or tears, which are quite transparent when first broken off. (For an excellent account of the production and gathering of it, see Aikins' Dict. art. Mucilage.)

Gum is dry, brittle, and insipid, and undergoes no change by exposure to the atmosphere, except that the action of light destroys the yellow colour. Its specific gravity varies from 1.300 to 1.490, water being 1.

It is readily soluble in water, and forms a viscid solution, which may be kept a long time without undergoing any change; but finally becomes sour, and exhales an odour of acetic acid. It is insoluble in alcohol and in ether, the former of which precipitates it from water, in opake white flakes.

It is separated from water, in a thick, curdy form, by subacetate of lead; and is thrown down by the red sulphate of iron, in the state of a brown semi-transparent jelly. Several other salts, also, have a similar effect. According to Dr. Thomson's experiments, the salts, containing mercury and iron at the maximum of oxidation, are the most efficient in precipitating gum. The oxides of copper, antimony, and bismuth, are also acted upon by it; for it prevents water from precipitating those oxides from their solutions in acids, in the state of sub-salts. A small proportion of gum renders, also, the acetate of lead much less easily precipitable by alkaline sulphates. (Quart. Journ. N.S. iii. 376.) The effects of re-agents on a solution of gum have been investigated by Dr. Bostock; and have been found to vary considerably in the different species of gum; for example, in gum arabic, cherry-tree gum, and linseed mucilage. (Nicholson's Journ. xviii. 28.)

Berzelius has examined the compound of gum arabic with oxide of lead, to which he has given the name of *gummate of lead*. (95 Ann. de Ch. 77.) He finds it to consist of

Gum	.....	61.75	.....	100.
Oxide of lead	..	38.25	.....	62.105
				—————
				100.

Gum is soluble in pure alkalis, and in lime-water, and is precipitated unchanged by acids. Of the earths, silica seems to have the strongest affinity for it; a solution of silicated alkali decomposing a very dilute solution of gum. (Thomson.) Dr. Duncan, jun., however, informs me, that this precipitate is produced only by solutions of the lighter coloured specimens of gum, which have different properties from those of darker colour. The precipitation, when it does occur, Dr. Bostock suspects to take place, only in consequence of the lime which gum contains. Hence oxalic acid, also, produces a precipitate from the solution of gum arabic.

Diluted acids dissolve gum unchanged, and the concentrated ones decompose it. Strong sulphuric acid converts it into water,

acetous acid, and charcoal; the last of which amounts to rather more than one-fourth the weight of the gum, and exhibits slight traces of artificial tan. Nitric acid dissolves gum with a disengagement of nitrous gas; and the solution, on cooling, deposits a little saccholactic acid. The production of *mucic* (saccholactic) acid, by the action of nitric acid, appears to be the characteristic property of mucilage; and Vauquelin even obtained this acid from the mucilage of linseed. Some malic acid is also formed; and by continuing the heat, the gum is changed by the nitric acid into oxalic acid, which amounts to nearly one-half the weight of the gum. Chlorine, transmitted through a solution of gum, changes it into citric acid. (Vauquelin. *Ann. de Chim.* vi. 178.)

Gum and sugar readily combine; and, by gentle evaporation of their mixed solutions, a transparent substance is obtained. From this, alcohol separates a part of the sugar, but the remainder continues in combination, and forms a substance resembling that of which the nests of wasps are composed.

Gum, when submitted to destructive distillation in a retort, yields an acid, formerly called the *pyro-mucous*, but now ascertained to be merely the acetic, holding in solution a portion of essential oil, and some ammonia, which last is disengaged on adding lime. Carbureted hydrogen and carbonic acid gases are also evolved; and in the retort there remains charcoal, mixed with lime and phosphate of lime.

By incinerating 100 parts of gum, Vauquelin obtained three parts of white ashes, consisting chiefly of carbonate of lime, but containing also some phosphate of lime and iron.

Respecting the varieties of vegetable mucilage, which appear to be pretty numerous and well marked, much valuable information may be obtained from the paper of Dr. Bostock, already referred to. Cherry-tree gum, tragacanth, and some other varieties, have been considered as forming a distinct vegetable substance, to which the name of *cerasin* has been given. It imbibes water, and swells very considerably in bulk, but is not at all soluble except in boiling water, from which it again separates on cooling in the state of a jelly. With nitric acid it yields abundance of mucic, malic, and oxalic acids; and the pyromucous acid, obtained by its distillation, gives much more ammonia than that from gum arabic. It appears then to contain more azote, and perhaps less oxygen and less carbon than gum arabic.

Gum arabic has been analyzed by Gay Lussac and Thenard, afterwards by Berzelius, and recently by Dr. Ure, whose experiments (Phil. Trans. 1822, p. 468) were made on gum of ordinary hygrometric dryness. Their results are as follows :

Carbon .....	42.23	....	41.906	....	35.25
Oxygen .....	50.84	....	51.306	....	58.90
Hydrogen .....	6.93	....	6.788	....	5.85
	100. (G.L.)		100. (B.)		100. (U.)

Saussure, in addition to these three elements, found also a minute quantity of nitrogen. (Thomson's Ann. vi. 431.) But this result is probably erroneous, since it does not agree with the experiments of any other person. Dr. Prout analyzed a very fine specimen of gum arabic, as it existed under the ordinary circumstances of the atmosphere, and found it (abstracting foreign matters) to consist of

Carbon .....	36.3			
Water .....	63.7	=	{	Hydrogen .. 7.08 Oxygen .... 55.92
	100.			

One hundred parts of the same gum exposed to a temperature between 200° and 212° for upwards of 20 hours, lost 12.4 parts. Hence its elementary constitution, when thus dried, would be nearly

Carbon .....	41.4			
Water .....	58.6	=	{	Hydrogen .... 51 Oxygen ..... 52.09
	100.			

These estimated results are confirmed almost exactly by actual analysis.

The same gum, exposed to a temperature between 300° and 350° for six hours longer, assumed a deep brown colour, and seemed to have suffered partial decomposition, though it had lost in weight only 2.6 per cent. more. Hence gum probably parts with the whole of the water not essential to its composition at 212° Fahr., provided that temperature be applied long enough.

The atomic constitution of gum, deduced on the supposition that gummate of lead is composed of two atoms of protoxide of lead and one atom of gum (which Dr. Thomson thinks most probable), will be as follows :

Carbon . . . . .	6 atoms	. . . . .	36	. . . . .	40.
Oxygen . . . . .	6 do.	. . . . .	48	. . . . .	53.34
Hydrogen . . . . .	6 do.	. . . . .	6	. . . . .	6.66
			90		100.

The proportions thus deduced, it may be remarked, approximate more nearly to the experimental results of Dr. Prout, than to those of any other analyst; but they must still be received as requiring confirmation.

### SECTION III.

#### *Vegetable Jelly.—Pectic Acid.*

Vegetable jelly may be obtained from the recently-expressed juices of certain fruits, such as the currant and gooseberry. When the expressed juice of these fruits is gently evaporated, and then allowed to remain, for some time, in a state of rest, it partly coagulates into a tremulous soft substance, well known by the name of jelly. The coagulum, washed with a very small quantity of water, is jelly nearly in a state of purity.

Vegetable jelly, unless when tinged by the fruit from which it has been obtained, is almost colourless; has a pleasant taste, and a tremulous consistency. It is soluble in cold water; but more copiously in hot, and the solution, if strong enough, again gelatinates on cooling. By long boiling it loses this last property, and is changed into a substance analogous to mucilage; hence the necessity, in preparing jelly from currants and other fruits, of not continuing the boiling too long, for this renders it viscid, and prevents it from coagulating. When dried, jelly is transparent. It combines readily with alkalis. Nitric acid converts it into oxalic acid, without disengaging any azotic gas. Its solution in water is precipitated by infusion of galls. Berzelius considers as identical with vegetable gelatine, and entitled to that name, a substance obtained from the gluten of wheat, which will be noticed in the section on vegetable gluten.

It is probable that jelly is nothing more than gum combined with vegetable acid; for when the coagulated jelly of acid fruits is placed on a sieve, an acid liquid passes through, leaving a tremulous mass, which dries into a hard transparent substance, resembling gum, and having most of its properties. The ultimate analysis of jelly has not been attempted.

*Pectic acid*.—Analogous to vegetable jelly, appears to be the substance described by Braconnot, which he obtains by the following process: The roots of carrots or turnips, reduced to a pulp by rasping, are submitted to the press, and the dry mass is washed repeatedly with distilled water, till it comes off colourless. It is then mixed with sufficient boiling water, to render it semi-fluid. About 50 parts of the residuum to 300 of water will be found good proportions. To these may be added caustic potash, or soda; of the former, for instance, as much as is equivalent to one part of potash prepared with alcohol, but the solution of either of these alkalis, prepared with lime, will answer the purpose. The mixture is to be boiled for a quarter of an hour, or till a portion of the thick liquor which is produced, taken out with a tube, is converted into jelly by an acid. The boiling liquid is then to be drained through a cloth, the mass washed with distilled water, and the several washings mixed together. The whole is thick, mucilaginous, and becomes a jelly on cooling. This alkaline pectate is next dissolved in water, and muriate of lime being now added, throws down an insoluble *pectate of lime*, which, being boiled with water acidulated with muriatic acid, is deprived of the earthy base and of a little starch. The whole is again thrown upon a drainer, and washed with distilled water, and pectic acid is obtained in a gelatinous form. It is liquefied with extreme facility by a few drops of solution of ammonia.

This mucilaginous solution, though perfectly insipid, sensibly reddens litmus paper. It may be employed in the preparation of jellies, but it is better to use at once the gelatinous acid. It appears to exist ready formed in roots, and in the juices of certain fruits, of gooseberries for example. It is deposited from a mixture of one-fourth of the juice of cherries, and three-fourths of gooseberries, and when washed with distilled water is pure, with the exception of a little colouring matter. In all the steps of its preparation, it is necessary to use water quite free from earthy salts, which are present in most spring-water, in sufficient quantity to precipitate it. This gelatinous acid, it appears, has been much employed in France as the diet of invalids, and is proposed as an effectual antidote against most poisonous salts, with the exception of corrosive sublimate and nitrate of silver. (30 Ann. de Chim. et de Phys. 96.)

## SECTION IV.

*Sugar and Oxalic Acid.*ART. 1.—*Sugar.*

Almost all the sugar, which is applied to the common purposes of life, is derived from a plant, the growth of hot climates, called *Arundo Saccharifera*. This plant produces strong canes, inclosing a soft pithy substance, which yield, by the compression of powerful machinery, a large proportion of sweet juice. The juice is evaporated in copper vessels, with the addition of a small quantity of slaked lime, the use of which appears to consist in its neutralizing a quantity of uncombined acid, that would be unfavourable to the crystallization of the sugar. A minute portion of lime remains in raw sugar, and according to Mr. Daniell, causes it to assume the clamminess, and soft feel, which characterize what is called *weak sugar*. It is desirable, therefore, to avoid using an excess of lime. During the evaporation of the cane juice, a thick scum is formed, which is continually removed. The juice passes successively from larger to smaller boilers, till at length, in the last of these, it becomes thick and tenacious. When this happens, it is emptied into shallow wooden coolers, where the syrup forms a mass of small irregular crystals, enveloped in a treacly fluid.

The whole mass is drained in hogsheds, in the bottoms of which holes are bored. The fluid, which separates, is called *melasses* or *treacle*; and the dried crystals are exported to this country under the name of *raw* or *muscovado sugar*. A gallon of juice yields on an average about a pound of raw sugar.

The subsequent process which sugar undergoes, with the view of bringing it to the white and beautiful form of *refined* or *loaf-sugar*, consists in its being redissolved in lime-water and in being boiled with a quantity of some coagulable substance, such as the whites of eggs or bullocks' blood. The proportions used are generally one part of fluid to three of sugar, and on this solution about fifty gallons, called a *skipping*, are put into a copper pan capable of holding about nine times that quantity. The pan, being covered only a few inches from the bottom, is in little danger of boiling over; and the higher the temperature, within certain limits, the less is the risk of this accident, be-



cause the highly expansive steam bursts the bubbles as soon as formed. A solution of this kind boils rapidly at  $230^{\circ}$  Fahr. ; and from this to  $240^{\circ}$  is the due temperature. If a solution of sugar be farther concentrated by the evaporation of the water, the thermometer rises to  $340^{\circ}$ . The sugar then begins to turn black, and at  $370^{\circ}$  it takes fire on applying flame to its vapour, and burns strongly, leaving a residuum of charcoal.

The clarifying substances, added to the heated syrup, coagulate into a thick scum, which rises to the surface, carrying along with it the principal part of the impurities of the sugar. After being evaporated to a due consistence, the syrup is let out into large conical earthen pots, with a hole at the apex of the cone, and each supported by an earthen jar. When the syrup has concreted into a solid mass, the plug is removed from the point of the cone, to allow the adhering liquid to drain off; and a mixture of pipe-clay and water is poured on the surface of the mould, and suffered to continue there four or five days. The moisture from this, slowly descending through the sugar, carries with it the remains of the darker-coloured syrup; and the whole loaf, after being dried in a stove, is obtained of the proper degree of whiteness.

Besides the juice of the cane, sugar may be extracted from several other vegetables. The juice, which flows spontaneously from incisions made in the American maple-tree, affords a quantity sufficient to render the process worth following. Ripe fruits contain sugar in considerable quantity, and, by long keeping after they have been dried, it appears in a granular state on their surface. The juice of the potato, the carrot, and still more remarkably of the beet (*beta vulgaris*, Linn.) yield a considerable proportion of sugar. To obtain it from the latter vegetable, the roots, softened in water, are to be sliced, and the juice expressed. It is then to be boiled down with the addition of a little lime till about two-thirds remain, and afterwards strained. These boilings and strainings are repeated alternately, till the liquid attains the consistence of syrup, when it is left to cool. The sugar thus extracted, retains somewhat of the taste of the root; but it may be purified by the operation already described as used for the refining of West India sugar, and it then loses its peculiar flavour. The quantity obtained varies considerably; but in general it may be stated at between four and five pounds from 100 pounds of the beet root, beside a

proportion of uncrystallizable syrup. In Germany, the expense has been calculated at about three pence per pound; but this estimate is probably under-rated. (See Chaptal on the manufacture of sugar in France, *Phil. Mag.* *xlvii.* 331; and an anonymous Essay in the *Quart. Journ.* *xxi.* 252.)

From the experiments of Proust (*Nich. Journ.* *xxi.* 356) it appears that a coarse sugar may be procured from grapes (of which many thousand tons are annually wasted in Spain), at the expense of about eight pence per pound; or, under favourable circumstances, even for five pence. In apples and pears, in the juice of liquorice, and in some other vegetable juices, sugar exists, but in a state of combination, which renders it essentially liquid, and prevents it from assuming a crystallized form. The sugar of grapes is not so white as cane sugar, but crystallizes more easily. Grape sugar has been analyzed by Saussure, and found to contain very nearly the same proportions of ingredients as starch sugar, stated under the article *fecula*. (See *Sect.* *ix.*) These two kinds of sugar agree, indeed, so closely as to their properties, that they probably constitute one species. Sugar from the cane and from beet differs from these, and from all other kinds of sugar, by containing a greater proportion of carbon. (*Ann. of Phil.* *vi.* 428.)

Sugar is produced in the process of malting, which consists in the conversion of starch into sugar; and starch, it will afterwards appear, may be converted into sugar by the action of sulphuric acid. Linen, also, by the successive action, first of concentrated sulphuric acid at common temperatures for 24 hours, and then with the addition of water and a boiling heat supported for ten hours more, is finally converted into sugar, exceeding the original weight of the linen by about one-seventh. If the process be limited to the action of the strong acid, gum and not sugar is obtained. (*Braconnot, Ann. de Ch. et de Phys.* *xii.* 182.) The sugar produced by the action of sulphuric acid on animal gelatine will be noticed in its proper place.

Beside pure sugar, there are other saccharine substances, that bear a considerable resemblance to it. *Manna* is the inspissated juice which flows spontaneously from incisions in the bark of a species of ash (the *fraxinus ornus*). Sugar has been discovered, also, by Fourcroy and Vauquelin, to enter largely into the composition of the juice obtained by pressure from the onion. Besides sugar, the juice of onions appears, also, to con-

tain a portion of mucilage and extract, to which its taste and other peculiar properties are owing. The same may, perhaps, be said of *honey*. When treated with nitric acid it was found, however, by Mr. Cruickshank, to give very little less oxalic acid, than was obtained from an equal weight of pure sugar. Proust has considered honey itself as of two distinct species. Common yellow honey is of an uniform consistence and viscid; but, besides this, there is a granulated white kind, which has a tendency to become solid. From the latter he obtained by alcohol a white saccharine powder, which he considers as agreeing more nearly with the sugar of the grape than with common sugar.

The root of *liquorice* (*glycyrrhiza glabra*) contains a peculiar saccharine principle, precipitable by acids. Robiquet employed the acetic for this purpose; but Berzelius prefers the sulphuric acid, added to the infusion of the root in hot water, till it ceases to cause precipitation. The sediment, consisting of the acid employed united with saccharine matter, is washed first with acidulated water, and then with pure water, till the washings come off tasteless. Alcohol, added to the drained matter, leaves undissolved the albumen, and takes up only the compound of acid with sugar. To the solution, carbonate of potassa or of soda is added in fine powder, and when it ceases to produce any effect, the liquid is decanted and evaporated. A slight excess of acid is advantageous, which may be obtained by setting apart a little of the alcoholic solution, and adding it to the alkalized liquid. The sulphate of potassa precipitates by standing, and the saccharine matter is obtained by cautious evaporation. It then forms a yellow transparent mass, which breaks into a coarse powder resembling amber. Heated with access of air, it swells, inflames, and burns with a clear flame, giving out smoke. In powder, it burns vividly, like pulverized resin or puff-ball. Its aqueous solution is precipitated by all acids, and the more so when they are added in excess. The precipitates have not an acid but a sweet taste, especially after being sufficiently washed. They are soluble in hot water, and pass to a yellow transparent jelly on cooling.

The saccharine matter of liquorice has, also, an attraction for alkaline bases, which renders it necessary to adjust very nicely the proportion of those that may be employed to disengage it from acids. Its alkaline combinations are soluble in

water, but very sparingly in alcohol. Those, which it affords with lime and baryta, are soluble, and are not precipitable by carbonic acid. With metallic salts it gives insoluble compounds. Acetate of lead throws down a precipitate, which, when decomposed by sulphureted hydrogen, gives a sulphuret of lead that remains in suspension, forming a black liquor, and thus prevents us from procuring in this way the pure saccharine matter.

The juice of wild liquorice (*polypodium vulgare*) was found by Berzelius to exhibit, with the same re-agents, a very different train of properties. (Ann. de Ch. et de Ph. xxxvii. 166.)

The following are the properties of pure cane sugar :

Sugar is perfectly white, and, when crystallized, somewhat transparent. It is hard and brittle. When two pieces are rubbed strongly against each other in the dark, a visible phosphorescence takes place. Its specific gravity, according to Hasenfratz, is 1.4045, according to Thomson 1.5629, but it is probably variable.

Pure sugar is not altered by exposure to the air, except that from a damp atmosphere it attracts a little moisture. Raw sugar, as is well known, is extremely deliquescent; and is rendered less saccharine by keeping. (See Quart. Journ. v. 32, and Phil. Trans. 1827, p. 372.)

Pure cane sugar appears to undergo no change at the temperature of boiling water; but at about 300° F. it begins to melt, and to assume the form of a dark brown liquid. By exposure to this temperature for six hours, it lost only 0.6 per cent., but its properties seemed to be permanently injured. (Prout.)

Sugar is soluble in an equal weight of cold water, and almost to an unlimited amount in hot water. The latter solution affords a liquid called syrup; from which, by long repose in a stove or warm room, transparent crystals of sugar separate, called *candied sugar*. Their form is that of prisms with four or six sides, bevelled at each extremity, or sometimes acuminate by three planes. They are composed, according to Berzelius, of 100 sugar + 5.6 water.

Alcohol dissolves, when heated, about one-fourth its weight of sugar. The solution, by keeping, deposits large crystals of sugar.

Lime-water renders sugar more soluble; and, reciprocally, sugar increases the solubility of lime. The liquid compound of sugar and lime is still sweet, but mixed with some astring-

gency. Alcohol precipitates white flakes, which appear to be composed of sugar and lime.

Alkalis unite with sugar, and destroy its taste. It may be recovered, however, unchanged, by adding sulphuric acid in equivalent quantity, and precipitating the alkaline sulphate by alcohol, which retains the sugar in solution. Sugar unites, also, with the alkaline earths; and is acted on by baryta so strongly, that it appears to undergo a kind of decomposition, and the baryta is immediately carbonated. Strontia acts in much the same manner as lime.

Sulphuric and muriatic acids act when concentrated upon sugar; charcoal is separated; much of the sugar destroyed; and what remains is rendered incapable of crystallizing. Nitric acid converts it, as will presently appear, into oxalic acid; and chlorine changes it into malic acid. Oxalic, acetic, and tartaric acid, prevent it from forming good crystals.

Sugar has the property of rendering oils miscible with water.

The sulphurets, hydro-sulphurets, and phosphurets, appear to have the property of converting sugar into a substance not unlike gum. (Thomson's Chem. iv. 214.)

Sugar has the property of decomposing several of the metallic salts, when boiled with their solutions. Sometimes it reduces the oxide to a metallic state, as in sulphate of copper. In other instances, as in the acetate of the same metal, it merely reduces the oxide to an inferior degree of oxidation. With protoxide of lead, it forms an insoluble compound, called improperly, by Berzelius, *saccharate of lead*, which he found to consist of

Sugar .....	41.74
Protoxide of lead.....	58.26
	100.

In one instance, Dr. Prout obtained this saccharate in beautiful crystals. By destructive distillation, sugar is converted into water, acetic acid, carbureted hydrogen, carbonic acid gas, and charcoal; and a little oil, with a large proportion of pyromucous acid, amounting to more than half the weight of the sugar, are also formed. No ammonia can be detected in the liquid products.

#### *Analysis of Sugar.*

According to Lavoisier, sugar is composed of 64 oxygen, 28

carbon, and 8 hydrogen: Gay Lussac, Thenard, and Berzelius, have analyzed it by combustion with chlorate of potassa, and Dr. Prout and Dr. Ure by peroxide of copper. The following are the results obtained by different chemists:

Carbon . . . .	42.47	..	44.200	..	42.85	..	43.38	..	41.8
Oxygen ..	50.63	..	49.015	..	50.80	..	50.33	..	51.7
Hydrogen..	6.90	..	6.785	..	6.35	..	6.29	..	6.5
	<u>100.*</u>		<u>100.†</u>		<u>100.‡</u>		<u>100.§</u>		<u>100.  </u>

The sugar analyzed by Dr. Prout in his recent experiments (Phil. Trans. 1827), was *sugar-candy*, purified by repeated solutions and crystallizations from water and alcohol, and then deprived of hygrometric water by exposure for some hours to a temperature of 212°. It was found to be constituted, as in the third column of the foregoing Table; or, viewing it as a compound of charcoal and water, of

Carbon .....	42.85
Water .....	<u>57.15</u>
	100.

In the sugars of commerce, and also in those varieties of sugar, which are obtained from other sources than the cane, considerable deviations from the above proportions were discovered by Dr. Prout, as will appear from the following Table: Those marked (v) are probably subject to slight variations of composition.

	Carbon.	Water.
Pure sugar-candy .....	42.85	.. 57.15
Impure ditto (v) .....	41.5 to 42.5	.. 58.5 to 57.5
East India ditto (v) .....	41.9	.. 58.1
English refined sugar .....	41.5 to 42.5	.. 58.5 to 57.5
East India ditto (v) .....	42.2	.. 57.8
Maple sugar (v) .....	42.1	.. 57.9
Beet-root sugar (v) .....	42.1	.. 57.9
East India moist sugar (v) ..	40.88	.. 59.12
Diabetic sugar .....	36 to 40?	.. 64 to 60?
Sugar of Narbonne honey ....	36.36	.. 63.63
Sugar from starch .....	36.2	.. 63.8

The sugar of commerce was in no instance found by Dr. Prout to contain more than 42.5 per cent. of carbon, and fre-

\* Gay Lussac.

† Berzelius.

‡ Prout, 1827.

|| Ure.

§ Crum, Ann. of Phil. N. S. v. 89, u.

quently, in those especially which are denominated *weak* or *low sugars*, considerably less. The weakest sugar analyzed by him was that of Narbonne honey, which, beside being deficient in carbon, seemed to have its elements more feebly held together than purer sugars, and to undergo a change of composition at 212° Fahr. Into all these varieties oxygen and hydrogen enter, in the proportions in which they form water; and as pure sugar, on account of its crystalline form, appears to constitute the most perfect and definite compound, Dr. Prout considers it as the type of all the varieties of sugar, and distinguishes it by the name of *the saccharine principle*.

Notwithstanding the pains that have been taken in the analysis of sugar, we are scarcely prepared to reduce its constitution to atomic proportions. In purified sugar-candy, for instance, the proportion of water to carbon is as 57.15 to 42.85, or as 9 to very nearly 6.75, instead of 6, which is the true number for carbon. At present, therefore, we must be content with deducing, from experimental results, what are the most probable atomic proportions of the elements of sugar, and these appear to be as follows:

Charcoal .....	6 atoms	.... 36	.... 44.44
Oxygen .....	5 do.	.... 40	.... 49.38
Hydrogen .....	5 do.	.... 5	.... 6.18
		81	100.

If derived from the compound of sugar with oxide of lead, on the supposition that this compound consists of an atom of each, and that the protoxide is represented by 112, the atomic weight of sugar will be 82 +, a coincidence which, though not perfect, is sufficiently near to strengthen the probability that sugar consists of 6 atoms of charcoal, 5 of oxygen, and 5 of hydrogen, and that 81 is its true representative number.

#### ART. 2.—*Oxalic Acid.*

Sugar is acidified by distillation with nitric acid. To six ounces of nitric acid, of sp. gr. from 1.46 to 1.5, contained in a stoppered retort, to which a large receiver is luted, add, by degrees, one ounce of refined sugar, coarsely powdered. A gentle heat may be applied during the solution. Nitrous gas will be disengaged in great abundance. When the whole of the sugar is dissolved, distil off a part of the acid. The

remaining liquor, which has a syrupy consistence, poured into a shallow glass or porcelain vessel, will form, after cooling and sufficient repose, regular crystals, amounting to 58 parts from 100 of sugar. These must be again dissolved in water and re-crystallized, and then laid on blotting-paper to dry.

Oxalic acid may be produced, also, by a similar treatment of gum, and of various other vegetables, and even of several animal products, such as silk, wool, &c.

The crystals of oxalic acid have the following characters :

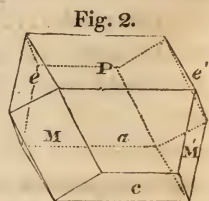
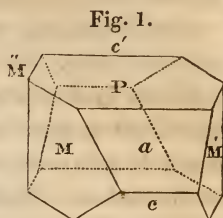
Their primary form is an *oblique rhombic prism*. There are distinct cleavages parallel to the planes  $M$  and  $M'$ , but others have not been observed. The crystals are usually attached by one of the lateral ends of the figure, in consequence of which the planes  $P$ ,  $a$ , and  $c$ , appear like lateral planes of a prism, and  $M$ ,  $M'$ , as its dihedral termination.

Fig. 1. exhibits the common form of the crystals ; and fig. 2, a modified form which sometimes occurs, and not unfrequently with only one of the planes  $e$  apparent at the lateral extremity, the other not being visible.

P on $M$ , or $M'$ .....	98° 30'
M on $M'$ .....	63 5
P on $a$ .....	129 20
P on $c'$ .....	103 15
P on $e$ , or $e'$ .....	107 00

They have a strong acid taste, and act powerfully on vegetable blue colours. One grain, dissolved in 3600 grains of water, reddens the colour of litmus paper. They dissolve in water at 62° ; affording a liquid of specific gravity 1.0314, which contains only 6 per cent. of crystallized acid. The crystals are taken up by an equal weight of hot water. They are soluble, also, in half their weight of boiling alcohol ; and, though sparingly, in ether. When exposed to the air, they effloresce, and become covered with a white powder.

The crystals of oxalic acid, when exposed to a moderate heat, swell, and are deprived of water. Not more than 28 parts of water, however, can be detached from 100 of the crystals,





without decomposing the acid. But, by combining the acid with oxide of lead, Berzelius found that the whole of its water might then be expelled by heat, and that the crystals consist of 58 real acid, and 42 water, approaching nearly to 1 atom of acid and 3 of water. Dr. Thomson, from his own experiments, (First Principles, ii. 103,) is led to consider them as composed of equal weights of water and anhydrous acid, or of 1 atom of acid + 4 of water. But Dalton and Prout agree with Berzelius in considering crystals of oxalic acid as composed of

1 atom of acid . . . . .	36
3 atoms of water . . . . .	27
	<hr style="width: 10%; margin: 0 auto;"/>
	63

Oxalic acid is a most virulent poison, and has frequently proved fatal, when taken by mistake for Epsom salt. From that salt, however, it may readily be distinguished, though not from other acids, by carefully tasting it in the smallest quantity sufficient for the purpose, when its sourness will be distinctly perceived. Or, without tasting it, if a few drops of water be placed on a slip of the dark blue paper which is commonly wrapped round sugar-loaves, and a small quantity of any substance suspected to be oxalic acid be added, that acid will be discovered by its changing the colour of the paper to a reddish brown. The solution also of a small quantity of oxalic acid in a tea-spoonful of water will effervesce with a little scraped chalk or common whiting; but neither of these effects is produced by Epsom salt.

The crystals slowly absorb chlorine, and are converted into a white substance having a saline appearance, which, when water is added, is changed into muriatic and carbonic acids. (Ann. de Ch. et de Ph. xix. 84.)

Oxalic acid is decomposed both by the oxides and chloride of gold, and in the former case with a disengagement of carbonic acid. (Ann. de Ch. et de Ph. xv. 125.) Peroxide of manganese, also, decomposes it, with an escape of carbonic acid.

A red heat entirely decomposes oxalic acid, and leaves only charcoal. During distillation, a considerable quantity of inflammable gas is obtained; and a portion of the acid is sublimed, unaltered, into the neck of the retort.

*Analysis.*—The analysis of oxalic acid, by combustion with chlorate of potassa, was performed by Gay Lussac and Thenard,

and with peroxide of copper by Berzelius and Ure. The following Table exhibits their different results; those of Gay Lussac and Thenard being corrected in the second column to exclude the water, which appears to have entered into the oxalate of lime employed in their experiment, in such proportion as to have been equal to one-fifth of its acid ingredient.

Carbon	.... 26.566	.... 33.217	.... 33.222	.... 33.33
Oxygen	.... 70.689	.... 66.290	.... 66.534	.... 66.66
Hydrogen	.. 2.745	.... 0.493	.... 0.244	
	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
	100.*	100.†	100.‡	100.§

The quantity of hydrogen in oxalic acid, deprived of water by combination with oxide of lead, is so extremely small, as not to amount to any atomic proportion. Döbereiner appears to have been the first to suggest, about the year 1815, that hydrogen is not an element of anhydrous oxalic acid, but that it is constituted of carbon and oxygen only; and he has added fresh evidence in favour of this view of its nature, in a short paper published in the *Ann. de Chim. et de Phys.* xix. 83. Dr. Thomson, also, by a careful analysis of the crystals, with peroxide of copper, finds, after making proper deduction for the water of crystallization, that the anhydrous acid consists of

Carbon	.... 33.34	.... 2 atoms	.... 12
Oxygen	.. 66.66	.... 3 atoms	.... 24
	<hr style="width: 100%;"/>		<hr style="width: 100%;"/>
	100.	Atomic Weight	36

Or it may be regarded as constituted of

Carbonic acid	..... 1 atom = 22
Carbonic oxide	..... 1 atom = 14
	<hr style="width: 100%;"/>
	36

*Oxalate of potassa* forms flat oblique four-sided prisms, terminated by dihedral summits, the lateral edges of the prism being usually bevelled. Its taste is cooling and bitter. At 60° Fahrenheit, it requires about twice its weight of water for solution. It is constituted of 1 atom of acid, 1 atom of base, and 1 atom of water. There is, also, a salt formed of the same base and acid, but with a considerable excess of acid, called

\* Gay Lussac and Thenard.

† Ditto, corrected.

‡ Berzelius, *Ann. of Phil.* v. 99.

§ Ure, *Phil. Trans.* 1822.

*super-oxalate* or *binoxalate of potassa*. It forms small white parallelopipeds, or rhomboids approaching to cubes. It has a pungent acid taste mixed with some bitterness. It requires for solution ten times its weight of water at  $60^{\circ}$ , and a still larger proportion of boiling water. It may either be formed artificially, or obtained from the juice of the *oxalis acetosella*, or of the *rumex acetosa*. When procured in the latter mode, it is sold under the name of *salt of sorrel*, or *essential salt of lemons*. The acid which it contains is double that in the oxalate; or, if we suppose 100 parts of potassa, and denote the quantity necessary to convert it into oxalate by  $x$ , then  $2x$  will convert it into binoxalate. Its constituents are,

2 atoms oxalic acid .....	72
1 atom potassa .....	48
2 atoms water .....	18

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Weight of its atom .....138

*Quadroxalate of potassa* may be composed in several methods. (See Berard, 73 Ann. de Chim. 271.) It was formed by Dr. Wollaston by digesting the binoxalate in a due proportion of nitric or muriatic acid. One half of the alkali unites with the mineral acid, and the other half remains combined with the oxalic acid. The salt forms beautiful crystals, which may be obtained pure by solution and a second crystallization. These are constituted of

4 atoms oxalic acid .....	144
1 atom potassa .....	48
7 atoms water .....	63

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255

If three parts by weight of the quadroxalate be decomposed by burning, and the alkali, which is thus disengaged, be mixed with a solution of one part of the crystallized salt, the latter is exactly neutralized. Hence the quadroxalate contains four times the acid that exists in the oxalate. The analysis of this class of salts, from which Dr. Wollaston (in the Phil. Trans. for 1808) drew a striking exemplification of the law of simple multiples discovered by Mr. Dalton, may be recapitulated as follows:

	Atom of base.	Atoms of acid.	Base.	Acid.	Equivalent number.
The oxalate consists of	1	+ 1	.... 48	+ 36	= 84
The binoxalate	..... 1	+ 2	.... 48	+ 72	= 120
The quadroxalate	.... 1	+ 4	.... 48	+ 144	= 192

*Oxalate of soda* readily crystallizes, and has a taste nearly resembling that of oxalate of potassa. When heated, it falls to powder, and loses the whole of its water, which is in less than atomic proportion, and therefore not essential. Soda forms, also, with oxalic acid, a *binoxalate*, but no *quadroxalate*. In the oxalate, supposing it to be constituted of 1 atom of base = 32, + 1 atom of acid = 36, together 68, 100 parts of soda must be combined with 112.53 parts of acid; in the binoxalate with 225.06. The latter salt contains, also, 3 atoms of water.

*Oxalate of ammonia* crystallizes in long transparent prisms. Its taste is bitter and unpleasant. At the temperature of 60°, 1000 grains of water dissolve only 45 grains of the salt, giving a solution of sp. gr. 1.0186. The solution is of great use as a re-agent; for it precipitates lime from almost all its soluble combinations, provided these be perfectly neutral, and discovers it even when in very minute quantity.

In the crystals of oxalate of ammonia, constituted of 1 atom of base = 17, + 1 atom of acid = 36, each atom of salt, supposed anhydrous, is united, according to Dr. Thomson, with 2 atoms of water. A super-oxalate or *binoxalate* of ammonia, also, exists, which is less soluble in water than the oxalate. In this, 1 atom of base is united with 2 atoms of acid and 8 atoms of water.

*Oxalate of lime* is extremely insoluble in water at all temperatures. It may be formed, either by dropping oxalic acid into lime-water, or by mingling the solution of any salt, with base of lime, with one of any of the soluble oxalates. When very slowly dried at the temperature of the atmosphere, it consists, according to Berzelius, of 4 atoms of water and 1 of oxalate; when more rapidly dried, of 2 atoms of water and 1 of oxalate, or of mixtures of those two hydrates in different proportions. Dr. Thomson finds that, when dried at a temperature not exceeding 100° Fahr., each atom retains two atoms of water. The anhydrous salt consists of

Lime . . . . .	1 atom . . . .	28 . . . .	43.75
Oxalic acid . . . .	1 atom . . . .	36 . . . .	56.25
		64	100.

Fresh precipitated oxalate of lime is soluble in nitric and muriatic acids; and hence, in the use of oxalate of ammonia or oxalic acid as a precipitant, it is necessary first to neutralize any excess of those acids, which the solution may contain. Laugier asserts that it is completely decomposed by pure potassa (Ann. of Phil. N. S. viii. 306); but it is probable that he was deceived by the use of an alkali not free from carbonic acid, for oxalate of lime is easily decomposed by alkaline carbonates.

*Oxalates of baryta and strontia* are white tasteless powders of very sparing solubility; but the former earth, with an excess of acid, forms a soluble super-oxalate. One hundred parts of strontia take by experiment 83.62 of oxalic acid for saturation. No super-oxalate exists with this base. The oxalate of baryta is more soluble than the strontitic salt. It consists of 1 atom of base, 1 atom of acid, and 3 atoms of water. A bin-oxalate of baryta may be formed, by adding oxalic acid to the white powder, which is precipitated by that acid from the watery solution of baryta. This salt, which shoots into small needle-formed crystals, has its elements so feebly combined, that it is decomposed by mere solution in water. It is constituted of 1 atom of base, 2 atoms of oxalic acid, and 3 atoms of water.

*Oxalate of magnesia* is a soft white powder, bearing a considerable resemblance to oxalate of lime. It is tasteless, and not sensibly soluble in water. Yet, when oxalate of ammonia is mixed with sulphate of magnesia, no precipitate falls, till the solution is heated and concentrated. When dried in the air, it consists of 1 atom of base, 1 atom of acid, and 2 atoms of water. The crystallized *bin-oxalate* is composed of 1 atom of base, 2 atoms of acid, and 7 atoms of water.

*Oxalate of alumina*.—Fresh precipitated alumina is soluble in oxalic acid; but the compound is not crystallizable, but forms when evaporated a yellowish pellucid mass. It has a sweetish astringent taste, and is composed of 1 atom of alumina, 1 atom of acid, and 3 atoms of water.

*Oxalate of manganese*.—Oxalic acid, digested with oxide of manganese, is partly decomposed; carbonic acid is disengaged with effervescence; and the manganese, reduced to the state of

deutoxide, unites with the oxalic acid. The oxalate of manganese is precipitated in the state of a white powder, which also appears on adding oxalic acid to the sulphate, nitrate, or muriate of manganese.

*Oxalate of zinc* appears on adding oxalic acid to the solution of sulphate, muriate, or nitrate of zinc, from which it throws down the whole of the metallic oxide, in the form of an insoluble oxalate composed of 1 atom of base, 1 atom of acid, and 2 atoms of water.

*Oxalates of iron*.—Oxalic acid unites both with the protoxide and peroxide of iron. The solution of the protoxide affords prismatic crystals of a green colour and sweet astringent taste, soluble in water, and composed of 55 acid + 45 oxide. By exposure to the air, in a liquid state, this salt is changed into *per-oxalate*, which is incapable of crystallizing, and has the form of a yellow powder, insoluble in water. The *per-oxalate* may, also, be formed by the direct combination of oxalic acid with peroxide of iron.

*Oxalate of tin* may be formed by the direct action of oxalic acid on tin. The solution yields prismatic crystals, which are soluble in water, and have an austere taste.

*Oxalate of cadmium*, formed by decomposing any salt of cadmium with the solution of an alkaline oxalate, is a white insoluble powder.

*Oxalate of antimony* is precipitated in small crystalline and insoluble grains, on adding oxalic acid to the solution of antimony in sulphuric acid.

*Oxalate of cerium*.—Oxalic acid and oxalate of ammonia precipitate the protoxide of cerium from its solutions, forming a white salt not soluble in an excess of acid, but soluble in liquid ammonia. With the peroxide, the precipitate is of a red colour.

*Oxalate of cobalt* is precipitated by oxalic acid from solutions of the metal, in the form of a red powder, insoluble in water without an excess of acid, but then forming a solution which is capable of yielding crystals.

*Oxalate of bismuth* may be formed either by decomposing the salts of bismuth with an alkaline oxalate, or by acting on the oxide with oxalic acid. It is a white insoluble powder.

*Oxalate of copper* appears in the state of a bluish green precipitate, when oxalic acid is added to nitrate, acetate, or sulphate of copper.

*Oxalate of lead* is best formed, by adding oxalic acid to solution of nitrate, or acetate of lead. It is nearly insoluble in water, unless an excess of acid be present. It has the property of detonating violently when heated in a glass tube with small pieces of potassium. (Phil. Mag. Feb. 1827.) According to Berzelius, it is composed of 24.54 oxalic acid + 75.46 oxide of lead, which agree as nearly as possible with an atom of each of its ingredients, *viz.*, 36 acid + 112 oxide.

*Oxalate of mercury* is precipitated by oxalic acid from nitrate of mercury, in the state of an insoluble white powder. This, when exposed to the light, becomes black, and detonates when heated. It enters into the composition of Howard's fulminating mercury.

*Oxalate of silver* may be formed by adding oxalic acid to nitrate of silver. Its colour is white, but it is blackened on exposure to the light by the reduction of its oxide.

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## SECTION V.

### *Native Vegetable Acids.*

Native vegetable acids are such as are found, ready formed, in plants or their fruits, and require, for their extraction, only pressure, and other simple processes, which can scarcely be supposed to produce any change in their nature or properties. The following are the principal ones hitherto discovered.

- |              |                |
|--------------|----------------|
| 1. Citric.   | 6. Benzoic.    |
| 2. Gallic.   | 7. Acetic.     |
| 3. Malic.    | 8. Prussic.    |
| 4. Tartaric. | 9. Phosphoric. |
| 5. Oxalic.   |                |

Besides these there are a few other acids, obtained only from particular vegetables, which may be classed together, because it may still be considered doubtful whether they are distinct acids, or only known acids having their properties disguised by combination with other vegetable substances. The complete alteration of properties, attending such combinations, in the acids termed sorbic, rheumic, &c., which for some time were ranked as new acids, but which were afterwards shown to be well-known acids united with other vegetable matter, should teach us caution

in admitting the claims of such substances to the title of new and peculiar compounds. Other vegetable acids, the results of more complicated processes, and produced by new arrangements of the vegetable elements, such as the succinic, camphoric, &c., will be described in connexion with the substances from which they are obtained.

#### ART. 1.—*Citric Acid.*

Citric acid exists in the expressed juice of the lime and lemon, along with a quantity of extractive matter and mucilage, and with variable proportions of malic and sometimes of acetic acid. The following process, for obtaining citric acid in a separate state, we owe to the ingenuity of Scheele. To the expressed juice of the lime or lemon, contained in a vessel of earthen ware, or white wood, add, very gradually, finely-powdered carbonate of lime (chalk or whiting), and stir the mixture well after each addition. An effervescence will ensue; and as long as this arises, on adding fresh portions of chalk, more chalk will be required. The exact proportion it is impossible to assign, on account of the variable strength of the acid juice. In general, from six to eight ounces of chalk are sufficient to saturate a wine-gallon of lime-juice. When it ceases to excite effervescence, and the liquor has lost its sour taste, allow the mixture to settle; decant the liquid, and add a quantity of water. Let the powder subside; the liquor be again decanted, and thrown away; and these operations repeated, till the water comes off quite tasteless and colourless. The insoluble precipitate consists of citric acid, united with lime; add to it slowly, while an assistant agitates the mixture constantly, a quantity of sulphuric acid, of the density 1.85 or thereabouts, equal to the weight of the chalk which has been employed, and previously diluted with 10 parts of water.—Let the acid and precipitate remain together 24 hours; during which time they must be frequently stirred with a wooden spatula. Then let the white sediment, which consists of sulphate of lime, subside; decant the clear liquor; add more water till it comes off tasteless; and mix all the liquors together. The solution, containing chiefly citric with a little sulphuric acid, and some mucilage, is to be evaporated first in a leaden boiler, and afterwards in shallow earthen dishes, placed in a sand-heat. Reduce the liquid to about one-fourth of its bulk by evaporation; separate the sulphate of lime, which will be deposited,



and again waste the liquor, by a heat not above  $212^{\circ}$ , to the consistence of syrup. Brown crystals will form on cooling, which must be set to drain; and the remaining liquor, when again evaporated repeatedly, will continue to yield fresh crystals. To purify these, let them be dissolved in water; and the solution be again evaporated. After the second crystallization, their colour will be improved; but it will require three or four crystallizations to obtain them perfectly white and well formed. In this state, they are the pure citric acid.

The proportions, which I have recommended for the preparation of citric acid, differ a little from those of Proust. (*Journ. de Phys.* lii. 366.) Four ounces of chalk saturated, he found, 94 ounces of lemon-juice; and the citrate of lime weighed seven ounces four drachms. But the four ounces of chalk, or 32 drachms, contained only 18 drachms of lime: and, from the analysis of citrate of lime, it appears to contain 63.8 parts of citric acid in 100. Hence the seven ounces four drachms contained  $41\frac{1}{4}$  drachms of citric acid. But to expel the carbonic acid completely from four ounces of chalk, five ounces of sulphuric acid of commerce were found necessary. This proportion, therefore, he employed in decomposing the citrate of lime. Six ounces of the citrate, by two crystallizations, gave  $3\frac{1}{2}$  ounces, or 28 drachms, of pretty large crystals; from whence it follows that the whole  $7\frac{1}{2}$  ounces would have given 4 ounces 3 drachms of crystallized citric acid. (*Phil. Mag.* x.)

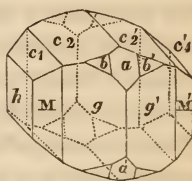
The preparation of solid citric acid on the large scale of manufacture requires an attention to a number of minute circumstances, which are stated at length by Mr. Parkes in the 46th volume of the *Philosophical Magazine*.

The citric acid, which is made for sale, is generally prepared from lime-juice; but it has been lately obtained economically, by M. Tilloy, from gooseberries (*Ann. de Ch. et de Ph.* Oct. 1828.) The quantity of solid citric acid, in a gallon of lime-juice, varies considerably. I have found it as high as twelve avoirdupois ounces in a gallon; but about six or eight ounces to the wine gallon is a fair general average. The only accurate method of ascertaining its proportion consists in adding, to a quantity of the juice, solution of pure potassa till saturation is produced. Liquid potassa, of a fit strength for this purpose, may be prepared by boiling two pounds of American potash with one pound of quicklime, previously slaked to a thin paste, and a gallon of

water, in an iron pot, during half an hour. The solution may be strained through calico, and reserved for use in well-stopped bottles. When employed as a test, one measure may be added to three measures of water; and it is proper to ascertain, by experiment, how much of this solution is requisite to saturate an avoirdupois ounce of white crystals of citric acid. It will then be easy, by saturating, with the same alkaline liquor, an aliquot part of a wine gallon of any sample of lime or lemon juice (judging of the point of saturation by test papers), to calculate what quantity of solid acid is contained in a gallon of the juice under examination. This, of course, implies that the juice is not contaminated with any other acid, which must be ascertained by the appropriate tests. By mere keeping, lime-juice is apt to pass to the acetous fermentation.

Pure citric acid forms beautiful transparent crystals, consisting of two four-sided pyramids joined base to base, or sometimes of rhomboidal prisms. Their primary form is a right rhombic prism, and the measurements, according to Mr. Brooke, nearly those which follow. The crystals, however, so speedily lose their brilliant surfaces when exposed to the air, or even when enclosed in a bottle, that the measured angles of the secondary faces are less to be relied upon, than those afforded by the cleavage planes.

M on M'	.....	101° 30'
M on <i>h</i>	.....	129 15
M on <i>g</i>	.....	163 23
<i>g</i> on <i>g'</i>	.....	134 45
<i>a</i> on <i>a'</i>	.....	111 50
<i>a</i> on <i>b</i>	.....	161 30
<i>h</i> on <i>c</i> <sub>1</sub>	.....	139 45
<i>h</i> on <i>c</i> <sub>2</sub>	.....	121 15
<i>c</i> <sub>1</sub> on <i>c</i> <sub>3</sub>	.....	161 30
<i>c</i> <sub>2</sub> on <i>c'</i> <sub>2</sub>	.....	117 30



An ounce of distilled water, at 60° Fahr., dissolves an ounce and a quarter of these crystals, or at the boiling temperature twice its weight. This solution is decomposed and becomes mouldy by keeping. The crystals do not attract moisture from the atmosphere; and when heated to a temperature just below what is sufficient to decompose the acid, they do not lose more than 7 per cent. of their weight. The real proportion of water

can only be determined, by uniting the acid with some basis, oxide of lead for example.

When treated with about three times its weight of nitric acid, the citric acid gives half its weight of oxalic acid. As the proportion of nitric acid is increased, that of the oxalic is diminished, till at length the latter disappears altogether, and acetic acid appears to be formed.

Citric acid is decomposed at a high temperature, and yields products which are constituted of carbon, hydrogen, and oxygen, in uncertain proportions. Gay Lussac and Thenard analyzed it by combustion with chlorate of potassa; Berzelius by peroxide of copper; and Drs. Ure and Prout by the same method. The difference between the results, exhibited in the first and second columns, Berzelius ascribes to the want of due allowance, by Gay Lussac and Thenard, for the water of crystallization.

Carbon ..	33.811	....	41.369	....	33.00	....	34.28	
Oxygen ..	59.859	....	54.831	....	62.37	....	60.96	
Hydrogen	6.330	....	3.800	....	4.63	....	4.76	
	<hr/>		<hr/>		<hr/>		<hr/>	
	100.*		100.†		100.‡		100.§	

Dr. Ure's determination, with which that of Dr. Prout very nearly accords, gives, for the crystals, 4 atoms of carbon + 5 of oxygen + 3 of hydrogen, and the equivalent number 67. Deducting two atoms of water, always detached by uniting the acid with protoxide of lead (or 2 atoms of oxygen + 2 of hydrogen), the composition of the anhydrous acid, appears to be 4 atoms of carbon = 24, + 3 of oxygen = 24, + 1 of hydrogen, and its equivalent number, therefore, to be 49. From the analysis of the crystals by peroxide of copper, as well as from the composition of citrate of lead, Dr. Thomson concludes that the true representative number for dry citric acid is 58, and for the crystals 58 + 18 = 76. (First Prin. ii. 122.) Such a number would nearly correspond with 4 atoms of carbon, 4 of oxygen, and 2 of hydrogen; but though coincident with the experiments of Berzelius, it must be considered as still somewhat doubtful. In describing the citrates, therefore, I have given the proportions derived from experiment, rather than from equivalent numbers not sufficiently established.

*Citrate of potassa.*—According to Vauquelin, 36 parts of crys-

\* Recherches, vol. ii.

† Berzelius, Ann. de Chim. xciv. 172.

‡ Ure, Phil. Trans. 1822.

§ Dr. Prout, Phil. Trans. 1827.

tallized citric acid, dissolved in water, require for saturation 61 of crystallized bi-carbonate of potassa; and the result is an extremely soluble and even deliquescent salt, composed in its dry state of  $55\frac{1}{2}$  acid and  $44\frac{1}{2}$  alkali.

*Citrate of soda* is a very soluble salt. Thirty-six parts of citric acid neutralize 42 of dry sub-carbonate of soda; and hence 100 parts of the citrate consist of 60.7 acid and 39.3 base.

*Citrate of ammonia*.—The same quantity of citric acid saturates 44 parts of sesqui-carbonate of ammonia; and affords a soluble and difficultly crystallizable salt, composed, in 100 parts, of 62 acid and 38 base.

*Citrate of baryta* is an insoluble salt of little importance.

*Citrate of magnesia*.—Thirty-six parts of crystallized acid neutralize 40 parts of common carbonate of magnesia. The salt is soluble, but not crystallizable.

*Citrate of lime*.—Crystallized citric acid, dissolved in water, requires an equal weight of chalk for saturation. The compound, when neutral, is insoluble; but with an excess of acid it becomes readily soluble. It was found by Gay Lussac and Thenard to consist of

	Expt.	=	Theory.		
Citric acid ..	68.83		1 atom	58	.... 67.6
Lime .....	31.17		1 atom	28	.... 32.4
	<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.			86	100.

*Citrate of zinc*, resulting from the action of citric acid on zinc, which it attacks with effervescence, forms small brilliant crystals, insoluble in water.

*Citrate of iron*.—Citric acid dissolves iron filings with effervescence. The solution, which is almost colourless, deposits citrate of iron in the state of a white powder. It has a sweetish and astringent taste; dissolves readily in water, but not in alcohol; and, when exposed in a moist state to the air, becomes first yellow and then olive, being converted into the *per-citrate*. This salt is deliquescent, and forms an olive-green solution, and is incapable of crystallizing.

There is also a *bi-citrate* of the protoxide, which is deposited, in a white crystalline form, during the solution of iron in citric acid. It has an acid and astringent taste, and does not undergo the farther oxidation of its base, nearly so soon as the neutral citrate.

*Citrate of copper.*—Citric acid dissolves oxide of copper at a boiling heat, and the solution yields light green crystals.

*Citrate of lead* is precipitated from acetate of lead by citric acid in the state of an insoluble powder. It contains, according to Berzelius, 34.18 acid + 65.82 base, proportions which confirm the equivalent number of citric acid, derived from its ultimate analysis, for 65.82 : 34.18 :: 112 : 58, very nearly.

These are the only citrates that have been particularly investigated.

#### *Pyro-citric Acid.*

M. Lassaigne gave this name to an acid, produced by the destructive distillation of citric acid. When citric acid is heated in a retort, it first fuses, and then parts with nearly the whole of its water of crystallization. The liquid products are of two different kinds: the one of an amber colour and oily consistence, occupies the bottom of the vessel; the other colourless and liquid like water, and floating over the former, has a decidedly sour taste. It is found, however, on examining the oily fluid, that, along with its bituminous taste, it has a strongly acid one; and on agitating it with water, and then allowing the mixture to stand, the water when decanted is distinctly acid. The oily fluid, left to itself, soon becomes acid again, and deposits white crystals which are also strongly acid. When again agitated with water, only a small portion reassumes the oily form; or, if kept under water, it is soon acidified.

The colourless liquid and the oily fluid contain an acid, which has properties differing essentially from those both of the citric and the acetic. It may be obtained pure, by first saturating it with lime, and then disengaging it by oxalic acid; or by decomposing the calcareous salt with acetate of lead, and treating the precipitate with sulphureted hydrogen. Its properties are the following: It is white, inodorous, sour to the taste, and a little bitter; difficult to obtain in distinct crystals, but presenting itself under a white mass formed by the interlacement of numerous fine needles. It is extremely soluble in alcohol and in water, the latter of which, at 50° Fahrenheit, takes up one-third its weight. It forms salts differing decidedly from those which result from the union of citric acid with the same bases; but yet it is remarkable that its capacity of saturation is exactly the same as that of citric acid. The results of its ultimate

analysis, effected by treating pyro-citrate of lead with oxide of copper, gives a perfectly different atomic constitution, *viz.*, carbon 47.5, oxygen 43.5, hydrogen 9. These results are not very remote from

Carbon . . . .	8 atoms	. . . . .	48	. . . . .	49.5
Oxygen . . . .	5 do.	. . . . .	40	. . . . .	41.2
Hydrogen .. 9	do.	. . . . .	9	. . . . .	9.3
			97		100.

#### ART. 2.—*Gallic Acid.*

This acid exists in the gall-nut, along with tan and other substances. In Sir H. Davy's experiments, 400 grains of a saturated infusion of galls, gave, by evaporation, 53 of solid matter; composed of nine-tenths tan, and one-tenth gallic acid. The acid, as was discovered by Scheele, may be obtained by exposing an infusion of galls in water to the air. A mouldy pellicle will form on the surface of the infusion; and, after some months' exposure, small yellow crystals will appear on the inside of the vessel. These crystals contain both tan and gallic acid. To purify them, they must be dissolved in alcohol, and the solution cautiously evaporated to dryness.

Gallic acid may also be procured by sublimation. Pounded galls are to be put, dry, into a large retort, and slowly and carefully heated. The gallic acid will rise, and be condensed in the neck of the retort in shining white crystalline plates. The process must be stopped before any oil comes over, as this would redissolve the crystals. This method is recommended by Deyeux as preferable to any other.

The gallic acid may be separated from the infusion of galls, by adding muriate of tin till the precipitate ceases to appear. This precipitate may be reserved for the experiments detailed under the article *Tan*. From the remaining solution the superabundant oxide of tin must be precipitated by sulphureted hydrogen gas, and the clear liquor, on evaporation, yields crystals of gallic acid. From one ounce of galls, according to Haussman, about three drachms of gallic acid may be thus obtained.

To separate gallic acid from the tan which accompanies it, Baruel has proposed to add to the infusion of galls a solution of white of eggs, till it ceases to occasion a precipitate; to eva-

porate to dryness the clarified liquor; and to add alcohol to the dry mass. From the alcoholic solution, the gallic acid may be obtained in crystals, by evaporation. (Thenard's *Traité de Chim.* 2d edit. and *Ann. de Chim. et de Phys.* x. 235.) Mr. Faraday has adopted a similar process, using gelatine instead of albumen, and applying it by boiling together bruised galls with about one-sixth their weight of clipped skins. (*Quart. Journ.* vi. 154.) All these methods, however, M. Braconnot is of opinion are inferior to that of Scheele, when modified as follows. He infused 250 grammes (each about  $15\frac{1}{2}$  grains) of bruised galls in rather more than two wine pints of water during four days, agitating from time to time; pressed out the liquor; filtered it through paper, and exposed the liquor to the air in a glass vessel, at a temperature varying from  $65^{\circ}$  to  $75^{\circ}$  Fahrenheit, for two months. A considerable quantity of gallic acid separated in crystals which were collected and pressed. The solid, thus obtained, consisted partly of gallic acid, and partly of a new acid insoluble in boiling water. The liquid, which passed through the cloth, was evaporated to the consistence of syrup, and at the end of 24 hours, more crystals were obtained, which were also subjected to pressure. The quantity of gallic acid amounted to 62 grammes, but it was mixed with an insoluble powder. The whole was boiled with about a pint and a quarter of water, and filtered; and about 10 grammes of a light fawn-coloured substance remained on the filter. The filtered solution deposited on cooling about 40 grammes of gallic acid, and, from the remaining liquid, about 10 grammes more were obtained by evaporation. M. Braconnot found also that gallic acid was developed, by keeping the bruised galls moistened and exposed to the air, and that an odour of alcohol was emitted during their decomposition. (*Ann. de Chim. &c.* ix. 184.)

By none of these processes, however, can gallic acid be obtained perfectly pure; for it is still contaminated with a small proportion of extract. To purify it, Deyeux advises its sublimation. Over a glass capsule, containing the impure acid, and placed in a sand-heat, another capsule is to be inverted, and kept cool. On the impression of the heat, the acid rises into the upper one, in the form of white needle-shaped crystals. By this process, the qualities, and probably the composition, of gallic acid, appear to undergo some change.

Braconnot finds that the gallic acid, prepared by his method,

and having a light fawn-colour, may be purified by dissolving 100 parts in 800 of boiling water, and adding 18 parts of animal charcoal (ivory-black) which has been washed with diluted muriatic acid. The materials are to be kept heated in a sand-bath for a quarter of an hour; and the liquor filtered through paper and suffered to cool, agitating it several times. The acid thus obtained is, after pressure, perfectly white, and occasions no precipitate in an infusion of gelatine. Redissolved in boiling distilled water, it forms small silky crystals of the most perfect whiteness.

The pure gallic acid has the following characters:

Its crystals, which are extremely minute, have for their primary form a *doubly oblique prism*; the measurements of which are given by Mr. Brooke, Ann. of Phil. N. S. vi. 119. They have a weakly acid and somewhat astringent taste.

Gallic acid burns with flame, when placed on a red-hot iron, and emits an aromatic smell. When distilled *per se* at a high temperature, it is decomposed, and yields the usual products of the destructive distillation of vegetable matter.

It is soluble in 24 parts of cold, or three of boiling water. The solution is decomposed by keeping, and acquires a mouldy pellicle on its surface. Alcohol, when cold, dissolves one-fourth, or an equal weight when heated. It is also soluble in ether. The watery solution reddens some blue vegetable colours; but Berzelius denies its action on the colour of turnsole. It effervesces with alkaline carbonates, but not with earthy ones.

Nitric acid converts the gallic into oxalic acid.

It unites with alkaline solutions without producing any deposit; but from watery solutions of lime, baryta, and strontia, it occasions a bluish precipitate. Of the combinations of earths with acids, it decomposes salts with base of glucina, yttria, and zirconia, a property distinguishing those earths from all others. Chevreul has shown that permanent compounds of gallic acid with potassa, soda, baryta, strontia, and lime, can only be obtained by operating out of contact with atmospheric air, the oxygen of which reacts, and destroys the acid. With potassa and soda, air being excluded, it forms soluble colourless salts, which, under the same circumstances, are decomposed by muriatic acid, affording muriates and pure gallic acid, which by exposure to oxygen gas is decomposed, and converted partly into carbonic acid.



Döbereiner finds that when a known quantity of gallic acid is dissolved in solution of ammonia, and is placed in contact with oxygen gas, sufficient of the latter is absorbed to convert all the hydrogen of the gallic acid into water. The gallic acid is thus converted into ulmin. (Ann. de Chim. &c. xxiv. 335.)

Gallic acid precipitates most metals from their solutions; gold, silver, and copper, of a brown colour; lead, white; mercury, orange; bismuth, yellow; and iron, deep black. It is incapable, however, according to Richter, of detaching iron from sulphuric acid, unless assisted by some body which has an affinity for sulphuric acid. The precipitate from solutions of iron is soluble in an excess of the acid entering into the solution. It forms the basis of ink, which, according to Deyeux, consists of carbureted oxide of iron, and gallate of iron.

The only analysis we possess of gallic acid is that of Berzelius (Ann. of Phil. v. 178). According to his experiments, it consists of

Carbon . . . . .	56.64
Oxygen . . . . .	38.36
Hydrogen . . . . .	5.
	100.

The atomic constitution, most nearly corresponding with these proportions, is the following:

Carbon . . . . .	6 atoms	....	36	....	57.14
Oxygen . . . . .	3 do.	....	24	....	38.10
Hydrogen . . . . .	3 do.	....	3	....	4.76
			63		100.

This agrees very nearly with the equivalent deducible from the composition of gallate of lead, which, according to Berzelius, consists of 173.97 protoxide of lead + 100 gallic acid; and  $173.97 : 100 :: 112$  (the equivalent of oxide of lead) : 63.92.

The *ellagic acid*, obtained by Braconnot, and as it would appear, before him, by Chevreul (Ann. de Chim. et de Ph. ix. 229), is a tasteless white powder with a shade of buff. It unites with potassa, soda, and ammonia, and forms difficultly-soluble salts, and precipitates lime-water. Vauquelin supposes that it exists ready formed in galls, and conceives it to be the same substance as that which is deposited when a strong infusion of

galls is immediately filtered and surrounded by ice. A greyish sediment falls, which, washed with cold water and filtered, he believes to be ellagic acid. It has probably the same constituents as gallic acid, slightly modified in their proportions. (Ann. de Chim. et de Ph. xxxvii. 175. N.)

### ART. 3.—*Malic Acid.*

This acid exists in the juice of apples, gooseberries, and of some other fruits, in which it is found mixed with the citric, and occasionally with other acids. It may be obtained by evaporating the juice nearly to dryness, and then adding alcohol, which dissolves the acids, and leaves the mucilage. To this solution of citric and malic acids in alcohol, chalk is to be added to saturation, and the precipitate to be washed with boiling water, which takes up the malate of lime, and leaves the citrate. The solution of the malate of lime may then be decomposed by sulphuric acid.

Or the juice of apples may be saturated with carbonate of potassa, and then mixed with a solution of acetate of lead, till the precipitate ceases. This precipitate is to be washed with water, and diluted sulphuric acid is to be added, till the liquor acquires an acid taste, unmixed with any sweetness. The fluid is to be filtered, to separate the sulphate of lead, and evaporated. It yields no crystals, but a thick liquor of a cherry-red colour. Braconnot objects to this process, that the acid, obtained by it, is contaminated with a mucilaginous matter intermediate between gum and sugar, which modifies its chemical properties.

Vauquelin has shown that the malic acid may be obtained advantageously from the juice of houseleek (*sempervivum tectorum*) by adding acetate or nitrate of lead, and decomposing the insoluble malate with sulphuric acid, added in slight excess. To remove the redundant sulphuric acid, Gay Lussac boils the liquor with a small quantity of litharge, and throws down the oxide of lead by a current of sulphureted hydrogen. He then evaporates to the consistence of syrup, and adds alcohol, which separates the malic acid from a portion of malate of lime. The alcohol is then distilled off at a gentle heat, and the residue dissolved in water. (Ann. de Chim. et de Phys. vi. 331.)

Malic acid may be formed, also, by the action of nitric acid on sugar. Equal weights of sugar and nitric acid are to be distilled together, till the mixture assumes a brown colour. The

oxalic acid may be separated by adding lime-water; after which, the remaining liquor is to be saturated with lime and filtered. On the addition of alcohol, a coagulum of malate of lime is formed, which may be dissolved in water, and decomposed, as before directed, by acetate of lead; and afterwards by sulphuric acid. This process, however, Mr. Donovan finds to be extremely uncertain and costly.

In 1815 Mr. Donovan discovered in the juice expressed from the berries of the *sorbus aucuparia*, or service tree (Phil. Trans. 1815), what he then considered as a distinct acid; and the experiments of Vauquelin and Braconnot appeared to confirm his conclusions. (Ann. de Ch. et de Phys. vi.) To procure it, the fruit of the *sorbus*, collected about the month of October, a little before it is perfectly ripe, is to be bruised in a porcelain or marble mortar, and submitted to strong pressure. Vauquelin recommends that the juice, thus obtained, should be allowed to remain 12 or 15 days in a moderately warm place. By the fermentation, which it thus undergoes, a quantity of viscid matter is deposited, which may be separated by filtration. The clear liquor may be mixed with a solution of acetate of lead, which affords a copious precipitate. This is to be washed on a filter, first with a large quantity of cold water, to free it from colouring matter; and next with repeated quantities of boiling water, the hot washings only being reserved in a series of glass jars. After some hours, they become opaque, and deposit crystals of singular lustre and beauty, resembling benzoic acid. Those, which have been formed in colourless washings, are to be collected on a filter, dried in the air, and preserved for a subsequent process.

The original mass, remaining on the filter, is next to be boiled for half an hour with a slight excess of diluted sulphuric acid; and when cold is to be filtered. The clear liquor is to be mixed, a second time, with acetate of lead; the precipitate washed as before with boiling water; and the crystals selected from the colourless washings only. The remaining mass is again to undergo the action of sulphuric acid as before. The crystals, thus collected, are to be boiled for half an hour with 2.3 their weight of sulphuric acid of the specific gravity of 1.090, supplying water as it evaporates, and taking care to keep the materials suspended, by stirring constantly with a glass rod. The clear liquor is to be filtered off, and poured into a tall and nar-

row glass jar. While still hot, sulphureted hydrogen gas is to be passed through it, till all the lead has been precipitated. The fluid is then to be filtered, and boiled in an open vessel, until the vapour ceases to blacken paper, on which characters have been traced with acetate of lead. The acid liquor thus obtained, when evaporated to a syrup, shoots on cooling into mamillary crystals, which have a very sour taste, and deliquesce in a moist atmosphere. Braconnot prefers obtaining the acid by the intermediation of lime rather than of oxide of lead, by which process he procures a larger proportion of acid.

By a subsequent train of experiments, Braconnot was led to conclude that the sorbic acid is essentially the same with the malic; for when divested of all impurities, it exhibited the same properties, and formed with bases precisely the same compounds. (Ann. de Ch. et de Phys. viii. 149.) The same conclusion has been drawn by Houton Labillardière. (Ibid. 214.) The identity of the acid, when obtained from different sources being thus established, it appears to be due to Scheele to distinguish it by the term *malic*, which he originally proposed for it.

The malic acid is liquid, and incapable of being crystallized; for, when evaporated, it becomes thick and viscid, like syrup. Its taste is very sour, but it is quite free from smell. It is difficult to obtain it free from colour; but, by a process somewhat tedious and complicated, Braconnot succeeded in preparing it quite white, from the juice of *sempervivum tectorum*. It is very soluble in water, and in alcohol. By keeping, it undergoes a kind of decomposition. Nitric acid converts it into oxalic acid. It unites with alkalis and earths. With lime it forms a salt which is almost insoluble in cold water, but readily soluble by hot; and in consequence of this last property, it may be easily separated from the oxalic, citric, and tartaric acids; all of which form, with lime, compounds that are insoluble even in boiling water. When perfectly pure, Gay Lussac has shown that it does not decompose either nitrate of silver, of mercury, or of lead; but from acetate of lead it throws down a precipitate, which is soluble in acetic acid, and even in boiling water.

When malic acid is heated out of the contact of air, it sublimes, and the sublimed crystals possess characters differing from those of the original acid. When thus altered, it has been called *pyromalic acid*. (See Lassaigue, 34 Ann. de Chim. et de Phys. 271.)

The sorbic acid, now proved to be identical with the malic, was analyzed by Dr. Prout, not *per se*, but in combination with lead, with lime, and with copper. (Phil. Trans. 1827.) It was found, abstracting water not essential to its composition, to consist of

Carbon .....	40.68	=	6 atoms	24
Oxygen .....	13.56	=	1 atom	8
Water .....	45.76	=	3 atoms	27
<hr style="width: 20%; margin: 0 auto;"/>				
100.			Atomic Wt. 59	

The probability that 59 is the true equivalent, is strengthened also by Vauquelin's analysis of sorbate or malate of lime, which gives 57.84 for the equivalent of malic acid, a difference not greater than might be expected from unavoidable errors of experiment.

*Malate of potassa* is deliquescent, very soluble, and not crystallizable. The bi-malate forms crystals which are permanent, soluble in water, but insoluble in alcohol.

*Malate of soda* resembles very closely in its properties the foregoing salt.

*Malate of lime*.—The neutral malate of lime is an insoluble salt, which may be obtained by adding lime-water to a solution of the super-malate. The latter salt is chiefly formed when carbonate of lime is added to malic acid. It has an acid taste; is soluble in water, but not in alcohol; and, when evaporated to dryness, assumes the appearance of gum. Malate of lime is often found in malic acid, and gives it the property of precipitating nitrate of lead.

*Malate of baryta* resembles the foregoing salt in its properties.

*Malate of strontia* is more soluble than the two foregoing malates, for strontitic water is not rendered turbid by malic acid, which precipitates lime and baryta from water.

*Malate of magnesia* forms permanent crystals, soluble in 28 times their weight of water at 60°.

*Malate of alumina* is precipitated, in an almost insoluble form, when malic acid is added to salts with base of alumina. Hence Mr. Chenevix proposed this acid as a means of separating alumina from magnesia; but the method has not been generally adopted in practice.

*Malate of iron* forms a brown solution which is not crystallizable.

*Malate of lead* is immediately precipitated on pouring malic acid into solution of acetate of lead, and on adding acetate of lead to any liquid containing malate of lime. It is soluble in weak nitric acid and acetic acid. According to Mr. Donovan, it is capable either of existing in a neutral state, or of uniting with an excess of either acid or base; but this is not consistent with the experience of Vauquelin. Gay Lussac (Ann. de Chim. et de Phys. vi. 332) suggests that a triple compound probably exists of malic acid with lime and oxide of lead.

The combinations of malic acid with other metallic oxides have not yet been investigated.

#### ART. 4.—*Tartaric Acid, and its Combinations.*

The tartaric acid is generally obtained from the bi-tartrate of potassa (purified cream of tartar) by the following process:

Let 100 parts of finely-powdered cream of tartar be intimately mixed with from  $26\frac{1}{2}$  to 30 parts of pulverized chalk. This is best done by grinding them together in a mortar, and passing the mixture through a sieve. Let the mixture be thrown, by spoonfuls, into eight or ten times its weight of boiling water; waiting for the cessation of the effervescence, which is produced by each addition, before any more is thrown in. This method I find preferable to the entire solution of the cream of tartar in the first instance, which requires a very large quantity of water. If it should appear, from the effect of the liquor on litmus paper, that the chalk has not been added in sufficient quantity, more may be gradually used, till the colour of the litmus is no longer reddened.

By this operation, a quantity of insoluble tartrate of lime will be formed, which is to be allowed to subside, and washed with abundance of cold water. To the tartrate of lime, diffused through a sufficient quantity of water, concentrated sulphuric acid may be added, equal in weight to the chalk which has been employed. The mixture may be allowed to stand for 24 hours, during which it should be frequently agitated. Assay a little of the clear liquor, by pouring into it some solution of acetate of lead. A copious precipitate will be formed, which may either consist of tartrate of lead, or of a mixture of tartrate with sulphate of lead. To determine this, add diluted nitric acid, which dissolves the tartrate but not the sulphate. A small quantity of uncombined sulphuric acid, though not necessary,

does no harm; but a large excess of that acid is injurious, from its reacting on the tartaric acid, when heat is applied in the subsequent stages of the process. The deficiency of sulphuric acid, if enough has not been used to decompose all the tartrate of lime, should be supplied by adding more; or a redundance of it removed by the addition of a little chalk. The evaporation of the solution may now be carried on, in a manner precisely similar to that directed for the citric acid; and the crystals purified by a second solution and evaporation.

The liquor remaining, after the addition of chalk, consists of the neutral tartrate of potassa. It may be decomposed by mixing it with solution of muriate of lime, till no farther precipitation ensues. An insoluble tartrate of lime falls down, which, after being well washed, may be decomposed by sulphuric acid. Or the tartrate of potassa may be evaporated to dryness, and reserved for other purposes.

Quicklime has been recommended as a substitute for chalk in this process; but I have never found that it could be employed with any advantage; for a quantity of caustic potassa is set at liberty by its action, which dissolves the tartrate of lime, and prevents it from precipitating. When chalk is employed for saturation, that part of the acid only is neutralized, which constitutes the *bi*-salt; but with quicklime the operation is carried still farther, and the neutral tartrate, also, abandons its acid.

The tartaric acid forms regular crystals, the primary form of which is an oblique rhombic prism. Fig. 1 exhibits the crystals as usually modified, with the planes symmetrically placed. Fig. 2 exhibits the same modified form, with the planes irregularly disposed as they appear in most of the crystals, the corresponding planes in both being marked with the same letters. This affords another instance of irregularity, which renders it not easy immediately to perceive the relations of the several planes to each other.

Fig. 1.

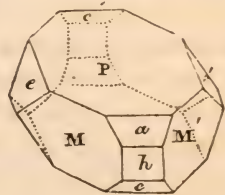
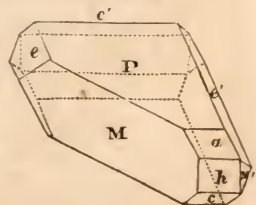


Fig. 2.



P on M, or M' .....	97° 10'
M on M' .....	88 30

P on <i>e</i> , or <i>e'</i> .....	128° 15'
P on <i>a</i> .....	134 50
P on <i>h</i> .....	100 47
P on <i>c'</i> .....	122 45

Their sp. gr. is 1.5962. They melt at a heat a little exceeding 212° into a fluid which boils at 250°, and leaves a semitransparent mass on cooling, slightly attractive of moisture from the air, though the original crystals were not deliquescent.

The crystals require for solution five or six parts of water at 60° Fahrenheit; but are much more soluble in boiling water. The solution, which, if saturated, has the sp. gr. 1.230, acquires, if diluted, like that of most other vegetable acids, a mouldy pellicle by keeping. The crystals were found by Berzelius to consist of 83.75 acid + 11.25 water.

Bergman exposed tartaric acid to distillation with nitric acid, in the manner practised for obtaining oxalic acid, but without being able to produce the latter acid. Hermbstadt, however, by using a very concentrated nitric acid, succeeded in converting the tartaric into the oxalic acid, and from six drachms of the former obtained four drachms and two scruples of the latter. Westrumb, also, was successful in the same attempt, and adds that the tartaric acid may be changed into the acetic by digestion with water and alcohol.

Tartaric acid has been analyzed by Gay Lussac and Thenard, by Berzelius, and by Dr. Ure, and their results are contained in the following Table. One hundred parts consist,

	Carbon.	Oxygen.	Hydrogen.
According to Gay Lussac, of 24.050	.... 69.321	.... 6.629	
———— Berzelius, of ..	35.98	.... 60.28	.... 3.74
———— Ure, of .....	31.42	.... 65.82	.... 2.76

The disagreement of the two first series of results with each other is occasioned, probably, by part of the water of crystallization having been attached to the acid analyzed by Gay Lussac and Thenard, which would increase the proportions of oxygen and hydrogen. The most probable atomic constitution of anhydrous tartaric acid appears to be the following:

Carbon .....	4 atoms ..	24	....	36.36
Oxygen .....	5 do. ..	40	....	60.61
Hydrogen ..	2 do. ..	2	....	3.03
		<hr/>		<hr/>
		66		100.



And the crystals are probably composed of

Anhydrous acid	1 atom	.... 66	.... 88.16
Water	1 atom	.... 9	.... 11.84
		75	100.

This view is confirmed by the analysis of Dr. Prout (Phil. Trans. 1827), and by the corrected one of Dr. Thomson, whose former experiments, it appears, had been made on a specimen of the crystallized acid, containing more than its due quantity of water. (First Princ. ii. 115.)

*Tartrate of potassa*, called formerly *soluble tartar*, may be obtained by adding sub-carbonate of potassa either to cream of tartar, or to the solution of the crystallized acid, till all effervescence ceases; or by evaporating the liquid which remains after adding chalk to the solution of bi-tartrate of potassa in preparing tartaric acid. According to Von Packen 120 grains of sub-carbonate require for saturation 112 of pure tartaric acid. Mr. R. Phillips finds that 100 parts of cream of tartar require for neutralization  $43\frac{1}{2}$  of sub-carbonate of potassa. The resulting salt is very soluble, and even deliquescent. It forms large crystals, the primary form of which is a right oblique-angled prism. (Brooke, Ann. of Phil. N. S. vii. 161.) These contain two atoms of water of crystallization, which may easily be driven off by heat. When anhydrous, it consists of

Tartaric acid	1 atom	.. 66	..... 57.90
Potassa	1 atom	.. 48	..... 42.10
		114	100.

*Super-tartrate, or bi-tartrate of potassa*.—If into a solution of the neutral tartrate of potassa we pour a solution of tartaric acid, a white powder falls down in great abundance, which is a compound of the neutral salt, and an additional proportion of acid. The tartaric acid, in this double proportion, even separates potassa from the mineral acids. Thus, by adding tartaric acid to the muriate of potassa, we obtain a precipitate of the bi-tartrate of that alkali.

The substance, which is known in commerce under the name of *tartar*, is an impure variety of this salt. When purified by solution and recrystallization, it affords white crystals, the form of which has been particularly described by Dr. Wollaston, and Mr. Brooke. (Thomson's Annals, x. 37. and N. S. vii. 161.)

These crystals, reduced into powder, become the *cream of tartar* of the shops.

Bi-tartrate of potassa has the specific gravity 1.953. It requires for its solution a very large quantity of water, not less than 60 parts at 60° Fahr., or 14 at 212°. Hence the solution in hot water deposits the salt, on cooling, so rapidly, and in such quantity, as almost to give the appearance of precipitation.

Bi-tartrate of potassa, it is observed by Gay Lussac, acts, in many cases, like a simple acid, and dissolves oxides that are insoluble in the mineral acids and even in the tartaric acid. (Ann. de Ch. et de Ph. iii. 281.) He proposes its use, therefore, in mineral analyses.

From the experiments of Berzelius, the composition of bi-tartrate of potassa may be stated at

Acid	.....	70.45	.....	100.
Potassa	.....	24.80	.....	35.2
Water	.....	4.75		
		<hr/>		
		100.		

The proportions, most consistent with the relative weights of the acid and base, are, exclusive of water,

Tartaric acid, 2 atoms	....	132	.....	73.89
Potassa	....	48	.....	26.11
		<hr/>		
		180		100.

In the bi-tartrate is found also a quantity of water, which appears essential to the constitution of the salt; for it cannot be separated by heat without decomposing the acid. Its proportion, indeed, is as nearly as possible that of an atom, for 95.25 : 4.75 :: 180 : 9, very nearly. We may consider the crystallized bi-tartrate then as constituted of 1 atom of bi-tartrate + 1 atom of water, though the proportion of water is stated by Dr. Thomson to be 2 atoms. (First Princ. ii. 264.)

When 100 grains of bi-tartrate are incinerated, so as to destroy the acid, the alkali obtained is exactly sufficient to neutralize 100 grains of the crystals dissolved in water; a proof that the potassa in the acidulous salt is combined with twice as much acid as in the neutral compound.

By the destructive distillation of 1000 parts of bi-tartrate of potassa, Fourcroy and Vauquelin obtained, exclusively of

gaseous products, of acid, and of charcoal (Ann. de Chim. lxiv. 43),

Pure dry sub-carbonate of potassa . . . . .	350
Tartrate of lime . . . . .	6
Silica . . . . .	1.2
Alumina . . . . .	0.25
Iron and manganese . . . . .	0.75

*Tartrate of potassa and soda* may be formed by neutralizing 24 parts of cream of tartar with 18 parts of sub-carbonate of soda. The resulting salt is well known from its being employed in medicine under the name of *Sel de Seignette*, or *Rochelle Salt*. The forms of its crystals, arising from the modification of a right rhombic prism, are represented by Mr. Brooke, Ann. of Phil. N.S. v. 451. It requires, for solution, about five parts of cold water, but much less at the boiling temperature. From the experiments of Vauquelin it appears to be composed of 54 parts of tartrate of potassa, and 46 parts of tartrate of soda. The proportions of 1 atom of tartrate of potassa + 1 atom of tartrate of soda would require that it should consist of

Tartrate of potassa . . . . .	53.73
Tartrate of soda . . . . .	46.27

---

100.

*Tartrate of potassa and antimony*.—This salt, commonly called *emetic tartar*, has already been fully described in the section on Antimony, page 86.

*Tartrate of soda*, formed by saturating tartaric acid with carbonate of soda, crystallizes in fine needles, which are soluble in an equal weight of cold water. They consist of 1 atom of acid, 1 atom of base, and 2 atoms of water. On adding a quantity of tartaric acid equal to that in the neutral salt, we obtain bi-tartrate of soda.

*Tartrate of ammonia* forms polygonal prisms, which have a bitter taste, are very soluble in water, and, on the addition of a farther proportion of tartaric acid, are converted into an insoluble bi-tartrate.

*Tartrate of lime* is formed, in the process for preparing tartaric acid, by adding carbonate of lime to a solution of bi-tartrate of potassa. It is white, tasteless, and almost insoluble in cold water, but soluble in 600 times its weight of boiling water, and in most of those acids that form soluble compounds with

lime. According to Berzelius (94 Ann. de Chim. 179), it consists, when dried at a gentle heat, of

Tartaric acid . . . .	50.55	. . . .	1 atom	. . . .	66
Lime . . . . .	21.64	. . . .	1 atom	. . . .	28
Water . . . . .	27.81	. . . .	4 atoms	. . . .	36
100.					130

And the anhydrous tartrate of lime will be represented by  $66 + 28 = 94$ .

*Tartrate of baryta* may be formed by mixing a solution of neutral tartrate of potassa with one of muriate of baryta. A compound falls down, which is insoluble in water, but dissolves in acetic acid, and in nitric and muriatic acids. It is anhydrous when carefully dried, and consists of an atom of each element. The *bi-tartrate of baryta* forms transparent crystals, consisting of 1 atom of base, 2 atoms of acid, and 2 atoms of water.

*Tartrate of strontia* may be formed also by double decomposition. It dissolves in 320 parts of boiling water, and crystallizes from its solution in rhomboidal prisms. According to Vauquelin it consists of 47.12 acid + 52.88 base.

*Tartrate of magnesia* is insoluble, and consists of 1 atom of base, 1 atom of acid, and 2 atoms of water. It is more saline to the taste than tartrate of lime, and is fusible by heat. There is also a *bi-tartrate* which is more soluble.

*Tartrate of alumina* may be prepared by acting with tartaric acid on fresh precipitated alumina. It is not crystallizable; but, when evaporated, forms a mass resembling gum, consisting of 1 atom of acid, 1 atom of base, and 1 atom of water.

*Tartrate of manganese.*—Tartaric acid, when heated in solution with black oxide of manganese, is decomposed, and carbonic acid is disengaged, a colourless solution of deutoxide of manganese being formed.

*Tartrate of zinc*, produced by the direct action of tartaric acid on zinc, is a salt of difficult solubility.

*Tartrate of iron* may be formed, either directly by acting on metallic iron with tartaric acid, or by mingling solutions of tartrate of potassa and proto-sulphate of iron. The compound forms lamellar crystals, which are sparingly soluble in water. By exposure to air, they pass to the state of *per-tartrate*.

*Tartrate of tin* has not been examined.

*Tartrate of tin and potassa* may be formed by boiling oxide

of tin in solution of bi-tartrate of potassa. It is very soluble, and is not precipitated by alkalis, either pure or carbonated.

*Tartrate of antimony and potassa* has already been described in the section on antimony.

*Tartrate of cobalt*.—Tartaric acid dissolves oxide of cobalt, and forms a red crystallizable salt.

*Tartrate of bismuth* is precipitated, as an insoluble white powder, from the salts of bismuth.

*Tartrate of copper* forms a blue sediment on dropping tartaric acid into sulphate or muriate of copper.

*Tartrate of lead* is best obtained by adding tartaric acid or neutral tartrate of potassa to acetate of lead. It is an insoluble white powder, and is constituted, according to the analysis of Berzelius, of

Tartaric acid . . . .	37.5	. . . .	1 atom	. . . .	66
Protoxide of lead ..	62.5	. . . .	1 atom	. . . .	112
	<hr style="width: 100px; margin: 0 auto;"/>				<hr style="width: 100px; margin: 0 auto;"/>
	100.				178

*Tartrate of mercury* is an insoluble white compound, which becomes yellow by exposure to the light. A triple salt may also be obtained by boiling in water six parts of cream of tartar and one part of oxide of mercury.

#### *Pyro-tartaric Acid.*

When tartaric acid, or bi-tartrate of potassa, is distilled alone in a retort, a large quantity of combustible gas escapes; an acid liquid passes over; and, towards the close of the process, a white sublimate appears, and concretes on the top of the retort. The acid liquor, when evaporated, also deposits crystals, and these, as well as the sublimate, are the *pyro-tartaric acid*. Its taste is extremely sour; it dissolves readily in water; and furnishes crystals by evaporation; and its crystals, when heated, first melt, and then sublime in a white smoke, leaving no residuum.

The watery solution does not immediately precipitate acetate of lead or nitrate of mercury; but, from the former solution, needle-shaped crystals are, after some time, separated. Its compound with potassa immediately decomposes acetate of lead, but does not, like tartrate of the same base, decompose the salts of baryta and lime; nor does it form, with an excess of acid, a difficultly soluble salt.

From these characters, which differ essentially both from those of tartaric and acetic acids, we may probably consider the pyro-tartaric as a distinct and peculiar acid. (See Ann. de Chim. lxiv. 42, or Nicholson's Journal, xxvi. 44.)

ART. 5.—*Benzoic Acid.*

This acid may be obtained from a substance termed gum benzöin or benjamin. It was formerly procured by putting a quantity of benzöin coarsely powdered, into an earthen pot, which was then subjected to a moderate sand-heat. The benzoic acid sublimed, and condensed in a cone of thick paper, with which the pot was covered. As thus obtained, however, it was stained by an empyreumatic oil. Another process, invented by Scheele, consists in pulverizing a pound and a half of gum benzöin with four ounces of quicklime, and then boiling them for half an hour in a gallon of water, constantly stirring. When cold, the clear liquor is poured off; and what remains is boiled, a second time, in four pints of water, the liquor being poured off as before. The mixed liquids, consisting chiefly of benzoate of lime, after being boiled to one-half, are filtered through paper; and muriatic acid is gradually added, until it ceases to produce a precipitate. Finally, after having decanted the liquid, the powder is dried in a gentle heat, and sublimed from a proper vessel, placed in a sand-bath, into cones of writing-paper.

Benzoic acid is found also in *storax*, *balsams of Peru and Tolu*, *vanilla*, *cinnamon*, in the urine of several graminivorous animals, and has been shown by Berzelius to be the characteristic ingredient of the acid obtained by the destructive distillation of tallow. Vogel lately met with it, in a crystallized state, between the skin and the kernel of the Tonquin bean, and in the flowers of the *Trifolium melilotus officinalis*. In the latter, Vogel thinks that it is sufficiently abundant to be advantageously extracted for use. (Annals of Phil. xvi. 227.) It is deposited, also, from oil of cassia and from the essential oil of bitter almonds. (Quart. Journ. xviii. 319.)

Benzoic acid has a peculiar and not disagreeable odour; and a taste in which nothing of acidity can be discovered, for it is rather sweet and aromatic; but it reddens the colour of litmus. Its crystals are soft and ductile, and cannot be reduced to powder. It is volatilized in white fumes by a moderate heat. It requires for solution about 24 times its weight of boiling

water, which, as it cools, lets fall  $\frac{1}{10}$ ths of what it had dissolved. It is soluble in alcohol. By leaving an alcoholic solution of it to evaporate spontaneously, it shoots into fine crystals, which are flat oblique prisms, perfectly transparent, and frequently an inch in length, and the twelfth of an inch in width, but so thin that two of their sides are scarcely perceptible. The angles of the prism are  $109^\circ$  and  $71^\circ$ . (Quarterly Journal, vi. 153.)

The most simple view of the constitution of benzoic acid, founded on the analysis of Berzelius, would represent it as constituted of 5 atoms of carbon, + 1 of oxygen, + 2 of hydrogen. But this does not agree with the equivalent deducible from the analysis, by the same chemist, of benzoate of lead, which is composed of 93.61 protoxide of lead, + 100 benzoic acid; numbers to which 112 and 119.64 are proportional. On the supposition, then, that neutral benzoate of lead contains an atom of each ingredient, the equivalent of benzoic acid is 119.64, or, in whole numbers, 120. Now this agrees very well with the following statement of the constitution of benzoic acid:

Carbon	..... 15 atoms	.... 90	.... 75
Oxygen	..... 3 do.	.... 24	.... 20
Hydrogen	..... 6 do.	.... 6	.... 5
		<hr style="width: 50px; margin: 0 auto;"/>	<hr style="width: 50px; margin: 0 auto;"/>
		120	100

Dr. Ure, by saturating benzoic acid with solution of ammonia, deduced 116 for the equivalent of that acid, which, according to his view, consists of

Carbon	..... 13 atoms	.... 78	.... 67.24
Oxygen	..... 4 do.	.... 32	.... 27.60
Hydrogen	.... 6 do.	.... 6	.... 5.16
		<hr style="width: 50px; margin: 0 auto;"/>	<hr style="width: 50px; margin: 0 auto;"/>
		116	100.

In calculating, however, from the ultimate analysis of the same vegetable substance by different persons, it appears to me that in general those results are to be preferred, by which the largest proportion of carbon is indicated; because it is more probable that too little carbonic acid should be found in the products of combustion than too much. In this instance, Berzelius remarks that the volatility of the benzoic acid renders it difficult to prevent a small quantity from escaping decomposition.

The compounds which this acid forms with alkaline and earthy bases, called *benzoates*, are fully described by Hisinger in the 40th volume of the Philosophical Magazine, and by Berzelius in the 90th volume of the Annales de Chimie, and those with metallic bases by Tromsdorff, in vol. xi. of that work. A few of the latter have, also, been noticed by Mr. Faraday. (Quart. Journal, vi. 159.)

*Benzoate of ammonia* may be obtained in feather-shaped crystals, which are very soluble, and even deliquescent. This salt has been recommended by Berzelius as an excellent reagent for precipitating peroxide of iron, which it throws down, from perfectly neutral solutions, of an orange colour; whereas the few other insoluble compounds, which this acid forms with the oxides of mercury, tellurium, and copper, are white. The crystals consist of 1 atom of acid, 1 atom of base, and 1 atom of water.

*Benzoate of potassa*.—The neutral benzoate forms feather-shaped crystals, which are soluble and deliquescent. With an additional proportion of acid, a bi-benzoate is produced, which crystallizes in small plates and needles. These require ten times their weight of water for solution, redden vegetable blues, and have an acid sweetish taste.

*Benzoate of soda*.—Its crystals are larger than those of the similar salt of potassa, and effloresce in the air. They are very soluble in water.

*Benzoate of lime* forms white shining crystals, requiring 20 times their weight of cold water for solution, but more soluble in hot water. It exists in the urine of the cow in considerable abundance.

*Benzoate of baryta*, crystallizable, and readily soluble.

*Benzoate of strontia*, little known, but probably soluble, because benzoate of ammonia does not precipitate muriate of strontia.

*Benzoate of magnesia*, crystallizable, and easily soluble.

*Benzoate of alumina* has a sharp bitter taste, is soluble in water, and deliquesces in the air.

*Benzoate of manganese* forms thin prismatic crystals, which are colourless and transparent, soluble in 20 times their weight of water, soluble in alcohol, and constituted of 23.08 oxide + 76.92 acid.

*Benzoate of zinc* exists in needle-shaped crystals, which are soluble in water and alcohol.



*Benzoate of iron* is an orange-yellow powder, insoluble in water. These characters apply to the compound formed by adding benzoate of ammonia to solution of peroxide of iron; but Tromsdorff states that oxide of iron is readily dissolved by an excess of benzoic acid, and forms yellowish crystals which are soluble in water and in alcohol. (Ann. de Chim. xi. 316.)

*Benzoate of copper* forms deep green crystals, which are soluble in water, but not in alcohol.

*Benzoate of lead.*—Berzelius describes two salts of lead, the *neutral benzoate*, which is a light crystalline powder, sparingly soluble in water, and constituted of 49.66 acid, 46.49 base, and 3.85 water; and the *sub-benzoate*, formed by treating the first-mentioned salt with solution of ammonia. The latter is insoluble, and consists of 26 acid + 74 base. If then 1 atom of acid be united with 1 of base in the neutral salt, we have in the sub-benzoate 3 atoms of base to 1 of acid.

For the benzoates of other metals, as they are of less importance, the reader is referred to the sources of information already quoted.

#### ART. 6.—*The Oxalic Acid*

Is found native in the juice of sorrel, forming a bin-oxalate, and, as appears from the experiments of Vauquelin, in the *Rheum Palmatum*. The neutral oxalate of lime, also, has been discovered in some plants. (Quart. Journ. N. S. No. 3, p. 214.)

#### ART. 7.—*Moroxylic Acid.*

Mr. Klaproth discovered this acid, combined with lime and extract, in small grains of a yellowish and blackish brown colour, which exude from the trunk of the white mulberry, *morus alba*, L. It was collected, by Dr. Thomson, from trees in the botanic garden at Palermo; and seems peculiar to those individuals that grow in hot climates. From its origin, it has been called, by Klaproth, *moroxylic acid*. (Nicholson's Journal, vii. 129.)

To obtain the acid in a separate state, the small grains, in which it occurs, were dissolved and decomposed by acetate of lead, and, to the insoluble precipitate, diluted sulphuric acid was added. From the liquid, fine needle-shaped crystals were obtained by evaporation, which had the taste of succinic acid;

were not altered by exposure to air ; dissolved readily in water and in alcohol ; but did not, like succinic acid or its salts, precipitate metallic solutions. When heated in a retort, these crystals first yielded a little acid liquor, and then sublimed unaltered, adhering in colourless and transparent crystals to the top and neck of the retort.

The compounds which this acid forms with bases have been called *moroxylates*.

#### ART. 8.—*Laccic Acid*.

This, in strictness, should be classed among animal acids. It is obtained from the white lac of Madras, from which, when liquefied, it oozes out in drops. It is in the form of a reddish liquor, having a slightly bitter saltish taste ; but, on evaporation, it shoots into acicular crystals, which are soluble in water, alcohol, and ether. It may be raised in distillation. It combines with carbonates of lime and soda, and excites effervescence. It precipitates lead and mercury from their solutions, but neither lime-water, nor the nitrates of silver or baryta. It assumes, however, a green colour with lime-water, and a purplish one with sulphate of iron. A full account of its properties, and of those of the substance that affords it, may be found in Dr. Pearson's paper in the Philosophical Transactions, 1794.

#### ART. 9.—*Phosphoric Acid*

Exists in almost all vegetable substances, and particularly in all the varieties of grain, not, however, in a free state, but in combination chiefly with potassa and lime. Hence the coal of almost all kinds of seeds affords phosphorus by distillation, a fact originally observed by Margraaf, and confirmed by the experiments of Saussure. (Nicholson's Journal, xxv. 279.)

#### ART. 10.—*The Prussic Acid*

Has been discovered in water distilled from bitter almonds, from the leaves of the laurel, from peach blossoms, and from the bark of the *prunus padus*. When the distilled liquid is neutralized with potassa, a crystallizable salt is obtained, the solution of which throws down prussian blue from the salts of iron. Vauquelin, also, obtained prussic acid by distilling water, with a very gentle heat, from the kernels of apricots. (Annales de Chimie, xlv. 206.) Robiquet found that when obtained

from the bitter almond, prussic acid is accompanied by two oils, one which crystallizes by the contact of air, while the more volatile one is not susceptible of crystallization. The latter is extremely deleterious, while the crystals are nearly inert.

ART. 11.—*Boletic Acid.*

This acid was first obtained by Braconnot, from the juice of the *boletus pseudo-ignarius*. (Thomson's Annals, ii. 469.) The juice was boiled, filtered, and evaporated cautiously, to the consistence of syrup. This was repeatedly digested in alcohol; the insoluble portion was dissolved in water, and precipitated by nitrate of lead. The white precipitate, thus obtained, was mixed with water, and decomposed by sulphureted hydrogen gas. The liquid, being evaporated, yielded crystals of *boletic acid*.

The crystals, when purified by solution in alcohol, and recrystallization, are white, and have the shape of irregular four-sided prisms. They require 180 parts of water at 68° to dissolve them, and 45 parts of alcohol. The aqueous solution reddens vegetable blues; precipitates nitrate of lead; and throws down the peroxide, but not the protoxide of iron, from its solutions. Nitrates of silver and mercury afford with it a white precipitate.

With the alkalis and earths, it unites, and forms a class of salts, which may be called *boletates*.

ART. 12.—*Zumic Acid.*

An acid was discovered, some years ago, by Braconnot, in vegetable substances, which have undergone the acetous fermentation. He first procured it from rice, which had been left, mixed with water, at a gentle heat, till it had become sour. When drained in a woollen bag, a liquid passed through, which gave acetous acid by distillation. Continuing the evaporation, almost to dryness, a gummy substance was left, having a decidedly acid taste. This was digested in alcohol; and the solution, evaporated to the consistence of syrup, became a granular crystalline mass with a strongly acid taste. It still, however, contained a salt with base of lime. The excess of acid was, therefore, neutralized by oxide of zinc; the salt obtained was decomposed by baryta; and the baryta precipitated by sulphuric acid. The liquor, being now carefully evaporated to a syrup, left an uncrystallizable, almost colourless, acid, nearly as strong to the taste as the oxalic. (86 Ann. de Chim. 84.)

With potassa and soda, this acid gave deliquescent salts, soluble in alcohol; and, with ammonia, a crystallizable salt. It formed, with lime, a salt, which required 21 times its weight of water for solution; with strontia, a salt soluble in 8 parts of water; with baryta, a gummy substance; and with magnesia, small granular crystals, which were not soluble in less than 25 parts of water.

Dr. Thomson, in the 5th edition of his *System of Chemistry*, proposed for this acid the name of *Zumic Acid*, from ζυμη, leaven; but its title to be considered as a distinct compound has been rendered doubtful, if not annulled, by the experiments of Vogel, who finds that it closely resembles the lactic (modified acetic) acid of Scheele and Berzelius. (*Ann. of Phil.* xii. 391.)

#### ART. 13.—*Rheumic Acid.*

A new acid was announced by Mr. Henderson as existing in the stems of garden rhubarb; but he candidly admitted the possibility of fallacy (*Thomson's Ann.* viii. 247), and Lassaigne afterwards proved (*Ann. de Ch. et de Phys.* viii. 402), that the supposed new acid is merely the oxalic, united with some impurities, which disguise its characteristic properties.

#### ART. 14.—*Kinic Acid.*

When yellow Peruvian bark is macerated in cold water, and the infusion concentrated and set apart for some time in an open vessel, a salt crystallizes from it, in square or rhomboidal plates, having no taste, soluble in five parts of cold water, and insoluble in alcohol. From this salt, first obtained by M. Deschamps, jun., of Lyons, Vauquelin separated the lime by oxalic acid, and concentrated the remaining liquor to the consistency of a syrup, which he set aside for a week, when, on touching it with a glass rod, it crystallized at once into divergent plates. Its colour was slightly brown; its taste extremely acid and rather bitter; and it was readily soluble in water. It is distinguishable from other vegetable acids by its forming a soluble salt with lime, and by its not precipitating silver or lead from their respective solutions. (*Ann. de Chim.* lix. 162.) MM. Plisson and Henry, jun. have since obtained this acid, by processes connected with the extraction of quinia, to be afterwards described. They have determined the properties of the compounds, both natural and artificial, which it forms with the new alkaloids, quinia and cinchonia,

which act towards it as salifiable bases. (Ann. de Ch. et de Phys. xxxv. 171.)

Beside the acids which have been described, there are a few others, the titles of some of which, to be considered as distinct compounds, are so doubtful that it may be sufficient merely to enumerate them.

The *meconic acid* is described in connexion with the substance, morphia, with which it is generally associated.

The *isaguric acid*, obtained by Pelletier and Caventou from *St. Ignatius's bean* (Ann. de Ch. et de Ph. viii.), approaches most nearly in its properties to the malic.

*Abietic acid* discovered by Baup in the resin of the *pinus abies*. (Quart. Journ. xxii. 398.)

*Pinic acid*, found by the same chemist, in the colophane of France, supposed to be derived from the *pinus maritima* (loc. cit.) and in Venice turpentine. (Id. viii. N.S. 445.)

The *menispermic acid* of Boullay has been shown by Casa-seca to have a very questionable title to be considered as a distinct acid. (Ann. de Ch. et de Ph. xxx. 314.)

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## SECTION VI.

### *Fixed or Fat Oils.*

These oils are extracted, by pressure, from certain vegetable seeds, which for the most part have two cotyledons, as the almond, linseed, poppy-seed, rape-seed, hemp-seed, &c., and from the pulp surrounding the stone of the olive. As thus obtained, they are liquid, almost tasteless, and for the most part inert on the animal body; but the oil expressed from the seed of the *croton tiglium* acts, in the quantity of a single drop, as a violent purgative, owing, it has been supposed, to its containing a peculiar principle called *tigline*. (Quart. Journ. xx. 231.)

Fixed oils are unctuous to the feel, and give a greasy stain to paper, which a moderate heat does not remove. They are generally combined with mucilage, to the spontaneous decomposition of which is partly owing the change, that oils undergo by keeping, called *rancidity*. In this state they are viscid, and contain an uncombined acid, which reddens vegetable blue colours. They are usually coloured, but may be deprived of

colour by digestion with animal charcoal. In their composition and properties, they so closely resemble animal oils, that they can scarcely be studied apart from the latter. In the present section some of their common properties will be noticed, and the peculiarities of animal oils will be more fully described on a subsequent occasion.

The specific gravity of vegetable fixed oils is commonly between that of alcohol and water; generally between .890 and .950, but varying in different oils and in different specimens of the same oil. Olive oil, for the most part is of the sp. gr. .913; oil of almonds and of linseed .932; and oil of palm .968. Hence these oils sink in alcohol, and float on the surface of the water. They cannot, by strong agitation, be brought to combine with water, but always separate on standing. When the seeds, however, which contain them, are rubbed with water, especially if a little sugar be added, an imperfect solution is obtained, called *an emulsion*. On adding an acid to this, the oil is detached, and floats on the surface.

The expressed oils of linseed and of olives, Mr. Brande finds, are very sparingly soluble in alcohol of specific gravity .820. Four ounce-measures of alcohol dissolve a drachm of linseed oil. Castor oil is perfectly soluble in every proportion in alcohol of .820, but not in weaker alcohol. (Phil. Trans. 1811. p. 265.) Four ounce-measures of sulphuric ether of specific gravity .7563 are capable of dissolving a fluid ounce and quarter of oil of almonds; a fluid ounce and half of olive oil; and almost any proportion of castor oil.

Some of the fixed oils congeal, or become solid, by a very moderate reduction of their temperature; and others, as palm oil, are permanently thick, or form a soft solid like butter, at the temperature of the atmosphere. When the congealed oil is subjected to pressure between folds of blotting-paper, a solid remains somewhat resembling wax, to which Chevreul has given the name of *stearin*; and the paper imbibes an oily fluid which he has called *elain*. These principles will be more fully described in speaking of animal fat. At present it may be sufficient to state that the proportions of elain and stearin differ in different varieties of vegetable oil, and even in different specimens of oil bearing the same name. In olive oil, at the temperature of 44° F., Braconnot found 72 elain + 28 stearin; in oil of sweet almonds 76 elain + 24 stearin; in rape oil 54 elain + 46 stearin.

By digestion with solutions of the fixed alkalis, vegetable fat oils are converted into soap. Of the nature of the changes which take place during saponification, we owe the first distinct view to Chevreul. They consist, not in the simple union of alkaline bases with the oils; but the oils themselves are decomposed, and their elements, are re-united into new compounds, chiefly acids. These combine with the alkaline bases in definite proportions, and form soaps, which may therefore be considered as true salts. The subject will be resumed in the section on animal oils.

By the action of alkalis, and still more by that of some metallic oxides (litharge for instance), a substance is developed, called by Scheele the *sweet principle*, and since termed *glycerine*. It is sweet to the taste, almost colourless, of the sp. gr. 1.252, and deliquescent. It is not susceptible of forming soap.

Soap is readily soluble in water, and in alcohol, and by gently distilling off the latter solvent, the soap is recovered in a transparent state. The watery solution is decomposed by acids, and by neutral salts with earthy bases. Hence hard waters, which contain earthy salts, curdle soap; their acid uniting with the alkali of the soap, and setting the oil at liberty. Soap is decomposed also by a solution of common salt, even when very dilute. Hence it cannot be employed in washing with sea-water. In this case, Vauquelin proposes to substitute a vegetable mucilage, such as that of the potato. (Quart. Journ. xxi. 179.) When a strong solution of soap is mixed with one of a metallic salt, a substance is formed, termed a metallic soap.

Fixed oils dissolve sulphur, and form a kind of *balsam*. They act also on phosphorus. Both these substances, when dissolved in the due proportion of hot oil, crystallize on cooling.

The properties of fixed oils are changed by boiling with metallic oxides, that of lead for example. The mucilage unites with this oxide, which probably gives up a portion of its oxygen to the oil, and the oil is rendered *drying*, and fit for the use of the painter. If the oxide be added in a larger proportion, the mass, when cold, composes a plaster.

Oils may also be rendered drying, by merely keeping them exposed to air; but the change is effected more rapidly by boiling them some time in an open iron pot, which gives them a higher colour and greater consistency. For some purposes, they are occasionally set on fire while boiling, and extinguished by covering the pot. This deprives them of their unctuousity

more completely than any other method; and it is always practised with oil intended for printers' ink. At a moderate temperature, they may be entirely volatilized in close vessels.

The condensible products of oil, which are partly solid and partly fluid, have been the subjects of an elaborate set of experiments by Bussy and Lecanu. (*Ann. de Chim.* xxxi. xxxiii. 107. xxxiv. 57.) By distillation from a retort at  $392^{\circ}$  F. they found that poppy oil emits a sharp and penetrating smell, and yields about  $\frac{1}{3}$  of its weight of a product which remains liquid till cooled to about  $68^{\circ}$  F. when it becomes a soft solid. Changing the receiver, a product comes over, which is liquid at common temperatures, and not acid. Lastly, when the retort acquires a red heat, a solid, of a colour resembling that of realgar is volatilized. One hundred grammes carefully distilled gave from four to five litres of gas, 1 to 2 grammes of charcoal, and 92 to 94 grammes of condensible products.

The first of the liquid products was found to consist of acetic, sebacic, oleic, and margaric acids, of an empyreumatic oil, and a volatile odorous oil. The sebacic acid was separated by the action of repeated portions of boiling water, from which it crystallizes on cooling. The remaining mass, which is half solid, when pressed between folds of bibulous paper at the temperature of the atmosphere, gives a white solid, (stearine?) fusible at  $134^{\circ}$  Fahr. and crystallizable, on cooling, into large needles of a brilliant pearly whiteness. The part absorbed by the paper consists of a volatile oil, a fixed oil, and oleic acid. It appears, then, that, by distillation, acids are evolved, precisely similar to those which are produced by saponification, and it is remarkable that no substance is capable of forming soap, that does not by distillation yield those acids. They are produced, still more abundantly, by distilling animal fats. Dupuy has shown that the products, from the same oily or fatty substance, vary greatly with the temperature at which the distillation is carried on. At a temperature below ebullition, tallow gives 30 per cent., and olive oil 20 per cent., of solid matter; but on raising the temperature considerably, only liquid products result. (*Ann. de Ch. et de Ph.* xxxii. 53.)

Fixed oils do not boil under  $600^{\circ}$  Fahr. An inflammable vapour arises from them under  $500^{\circ}$ , but this is condensible, and when rectified is highly volatile and inflammable. It does not appear that permanent gases are generated from oil under  $600^{\circ}$  Fahr.; but at that temperature, or a little above it, water



and olefiant and other varieties of carbureted hydrogen gas, are formed abundantly, with small proportions of acetic acid, carbonic acid, and carbonic oxide. Oil, transmitted through tubes moderately ignited, is wholly changed into gaseous products and carbonaceous matter.

Fixed oils are extremely combustible; and when burned in an apparatus, adapted for collecting the products of their combustion, they afford nothing beside carbonic acid and water. It may be inferred, therefore, that they contain carbon and hydrogen, the proportions of which, according to the experiments of Lavoisier, are 79 of the former and 21 of the latter. From this statement, however, oxygen is excluded, which it is certain that all fixed oils contain; for its presence is demonstrated by the following experiment of Sir H. Davy. When a globule of potassium is introduced into any of the fixed oils made hot, the first product is pure hydrogen, which arises from the decomposition of the water, absorbed by the crust of potassa during exposure to the atmosphere. If the globule be previously freed from this crust, carbureted hydrogen is disengaged, coaly matter deposited, and a soap is formed. To generate the alkali, however, which this soap contains, oxygen must necessarily have been supplied by the decomposition of the oil. Sir H. Davy has also found, in the products of the destructive distillation of oils by heat, a proportion of water, to the production of which oxygen is essential. (Phil. Trans. 1808.) Additional evidence of the presence of oxygen in oil has been supplied also by Gay Lussac and Thenard's analysis of olive oil, which they find to be composed of

Carbon ..... 77.213 Oxygen ..... 9.427 Hydrogen ..... 13.360 <hr style="width: 100%;"/> 100.	} or {	Carbon ..... 77.213 Water ..... 10.712 Excess of hydrog. 12.075 <hr style="width: 100%;"/> 100.
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Olive oil, then, probably consists of

Carbon . . . .	76	=	10 atoms	=	60
Oxygen ..	10	=	1 atom	=	8
Hydrogen	14	=	11 atoms	=	11
	<hr style="width: 100%;"/>				<hr style="width: 100%;"/>
	100		Atomic Wt.		79

Or, supposing each atom of carbon to be associated with 1 of hydrogen, it will contain 10 atoms of olefiant gas, + 1 atom of water

The action of acids, especially of the sulphuric, on oils, has been investigated, and fully described, in a memoir by M. Gaultier de Claubry. (Journal de Physique, 1815.)

Nitric acid acts upon them with great energy. In a small proportion, its chief effect is to render them thicker; when distilled with a larger proportion of acid, the oil is decomposed, and nitrous gas disengaged; oxalic acid remaining in the retort. Red and smoking nitric acid, when suddenly mixed with a fixed oil, especially with the addition of a little sulphuric acid, occasions a violent combustion. Chlorine gas, passed through fat oils, thickens them, and renders them tenacious like wax. *Acid soap* is best formed by uniting concentrated sulphuric acid with oil. It lathers with water like common soap, but can scarcely be considered as a permanent compound; and is of no practical use.

The fixed oils have a singular property, which has led sometimes to serious accidents. When mixed with lamp-black, or with any light kind of charcoal, and even with several vegetable substances, as cotton-wool, or flax, the mixture, after some time, heats spontaneously, and at length bursts into flame. This spontaneous combustion has sometimes been observed to take place in the waste cotton, which has been employed to wipe oil from machinery, and been thrown aside for a few hours. It has probably occasioned many of the calamitous fires, which have happened in cotton-mills, and for which no adequate cause could be assigned. (See Quart. Journal v. 367.)

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## SECTION VII.

### *Volatile or Essential Oils.*

With the exception of the oil from the rinds of the lemon and the orange, which are obtained by expression, the essential oils are procured, by distilling the vegetables that afford them, with a proper proportion of water. The oil either sinks to the bottom, or swims on the surface of the water, according to its specific gravity. If the distilled water be very long kept, Bucholz finds that the oil is converted into mucilage. The chemical history of the essential oils is still incomplete, and presents a field for new and interesting researches.

These oils have a penetrating and often a fragrant smell, and an acrid taste, which, however, is in many cases agreeable,

provided they are sufficiently diluted. Their colours vary exceedingly, not only in different oils, but in the same oil according to its age.

They are volatilized by a heat below  $212^{\circ}$  Fahr. Hence the spot, which they leave on paper, may be removed by holding the paper at a small distance from the fire; but the stains from expressed oils are permanent. In this way, their adulteration with fixed oils may be detected. The volatile oils are very combustible, and burn without requiring a *wick*, which the fat oils do not.

They can, with difficulty, be brought to unite with alkalis; and seem indeed to resist combination with those bases, until by oxygenation they are converted into resin. Hence the necessity for the long and tedious trituration of alkali with oil of turpentine, which is required to form the compound called *Starkey's soap*. On essential oil of cloves, M. Bonastre, however, has found that pure alkalis and alkaline earths have a distinct action. (35 Ann. de Ch. et de Ph. 274.)

They are all soluble in alcohol, but in different proportions. They do not unite with water. With the intervention of a little sugar, however, they are combinable, or rather perhaps miscible, in small proportion, with water.

When nitric acid is poured upon these oils, especially if it has been previously mixed with one-fifth or one-sixth of sulphuric acid, the mixture bursts into a violent flame. This experiment requires caution, as the inflamed oil is apt to be scattered to some distance. Several of them detonate, also, when rubbed with chlorate of potassa, and take fire when poured into chlorine gas.

Essential oils are thickened by long exposure to air. This is owing, as Dr. Priestley first proved, to their absorbing oxygen; a fact which accounts, in some degree, for the injurious effects of fresh-painted rooms. But they also undergo a material change when exposed to the light in close vessels; their colour deepens; they become more consistent and even unctuous; and their specific gravity is increased. In this case, too, the absorption of oxygen probably takes place, for the change is more complete, the more air is included in the vessel with the oil. Dr. McCulloch finds that by long keeping, some of the essential oils (that of roses, and still more that of aniseeds) are converted into a solid resembling spermaceti, which is almost inodorous. Other oils, that of turpentine, &c., are

changed by inspissation into a solid more like resin. (Quart. Journ. July 1829; see also Ann. de Ch. et de Ph. xxxi. 442.)

Potassium decomposes the volatile oils when heated. Alkali is formed; a small quantity of gas is evolved; and charcoal is deposited.

When digested with sulphur they unite with it, forming what have been called *balsams of sulphur*. These, when heated strongly, give a large quantity of sulphureted hydrogen gas.

Essential oils dissolve phosphorus at a digesting heat. When 1 part of phosphorus and 10 of camphor are triturated together, and then dissolved in oil of cloves or some other essential oil, a permanent solution is obtained called *liquid phosphorus*, which renders every thing that is rubbed with it luminous, without causing combustion.

One of the most useful and abundant of the essential oils is that of turpentine, called commonly *spirit of turpentine*. It is obtained by distilling turpentine and water, in due proportions, from a copper alembic. It is perfectly limpid and colourless, has a strong smell, a bitterish taste, boils at 316° (314° Despretz), and is extremely inflammable. It is the solvent which is employed in making a variety of varnishes, but for purposes of nicety it requires to be rectified by a second distillation. In submitting to this process a quantity of the essential oil which has been exposed a long time to the action of atmospheric air, an acid liquor is obtained at the close of the operation, holding in solution a peculiar substance which may be separated in the form of crystals by a temperature of about 20° F. (Ann. de Ch. et de Ph. xxxi. 442.) Another new substance has been obtained by M. Plisson from the essential oil of orange flowers, by the action of alcohol. It most resembles *myricine*, but differs from it in being more fusible, and in its relation to some solvents. From its sources Plisson has given it the name of *aurade*. (Ann. de Ch. et de Ph. xl. 83.)

Dr. Ure analyzed a specimen of oil of turpentine, sp. gr. 0.888, and found it to be composed of

Carbon 14 atoms . . . . .	84	. . . . .	82.35
Hydrogen 10 atoms . . . . .	10	. . . . .	9.80
Oxygen 1 atom . . . . .	8	. . . . .	7.85
	102		100.

When purified by alcohol, it had the sp. gr. 0.878, and ap-

peared to be compounded of carbon and hydrogen only, and to approach very nearly to the constitution of naphtha. (Phil. Trans. 1822.)

### *Camphor.*

Camphor is a white, semi-transparent, and highly inflammable solid, which in some properties resembles essential oils. It is obtained from the *laurus camphora*, in Japan, and other places in the East, by distilling the wood along with water. After being brought to Europe, it is refined by a second sublimation in vessels of glass, whose shape it takes. In this state it has a crystalline fracture, is brittle, has an aromatic odour, and a hot acrid taste. Its specific gravity is 0.988.

Camphor melts at 288° Fahr., and boils at 400°. It is volatile, and evaporates spontaneously, and condenses, in the upper part of any glass vessel in which it is kept, in hexagonal plates or pyramids.

It is insoluble in water, but communicates its flavour to hot water when triturated along with it, especially if a little sugar be added. It is soluble to a considerable extent in alcohol, which takes up 3-4ths of its weight. On adding water, the camphor is again precipitated. It is soluble also both in fixed and volatile oils, and in strong acetic acid.

Sulphuric acid was found by Mr. Hatchett to produce a complete decomposition of camphor, and to convert it into charcoal, a yellow oil, and a blackish brown resin analogous to artificial tan. (Phil. Trans. 1805.)

By the action of nitric acid, camphor is acidified. For this purpose, camphor is to be repeatedly distilled with four times its weight of nitric acid, till about 20 parts of acid have been employed. At each operation, the portion of camphor, which sublimes and escapes decomposition, is to be returned into the retort. The acid is susceptible of crystallization; the crystals effloresce in the air, and are soluble in 100 times their weight of cold, or in 11 times their weight of boiling water; they are combustible; and burn with a dense, aromatic smoke; they melt and sublime with a gentle heat, and dissolve in the mineral acids. They dissolve also in about six times their weight of cold alcohol, or to any amount in boiling alcohol; and are not precipitated by water. With alkalis and earths they compose a class of salts called camphorates. Fifty grains of the acid are saturated by 28 of carbonate of lime = 15.7 pure lime.

The ultimate analysis of camphor has been performed by Dr. Ure, who represents its constitution as follows :

Carbon .. . . .	10 atoms ..	60 .....	78.02
Oxygen .....	1 atom ..	8 .....	10.40
Hydrogen ....	9 atoms ..	9 .....	11.58
		<hr style="width: 10%; margin: 0 auto;"/>	
		77	<hr style="width: 10%; margin: 0 auto;"/>
			100.

A singular substance, very much resembling camphor in its sensible and chemical properties, may be obtained by passing muriatic acid gas through essential oil of turpentine, which absorbs about a third of its weight. The oil of turpentine becomes thick, from an abundance of a white crystalline substance which forms in it. This may be separated by draining off the liquid ; and is found rather to exceed the weight of the essential oil submitted to experiment. (Thenard, Mémoires d'Arcueil, ii.) It is white, crystalline, granular, volatile in a moderate heat, and has very much the smell of camphor. By exposure to the air, it soon loses its property of reddening vegetable blue colours. As to the theory of its production, Thenard is of opinion that no decomposition of the oil of turpentine takes place ; but that the muriatic acid unites to it entire. Ordinary camphor of commerce, he supposes, from analogy, to be a compound of an essential oil and a vegetable acid.

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## SECTION VIII.

### *Resins.*

Resins are the inspissated juices of certain plants, and are generally obtained by wounding their bark. Copal, or lac, may be taken as an example. Dragon's blood, guaiacum, mastich, elemi, anime, tacamahac, sandarach, labdanum, resin, and turpentine, are also varieties of this substance. Common resin, or *rosin*, is the substance which remains after the distillation of turpentine.

Resins have generally a yellow colour, and are imperfectly transparent. In specific gravity they exceed water. That of resin is 1.080. They are dry, brittle, and extremely inflammable, and emit during combustion a copious and dense smoke.

All the resins are fusible. Common resin melts at 156°, and

assumes the consistence of turpentine. If the heat be increased, it swells up, and becomes filled with bubbles, owing to a quantity of water, and probably of essential oil, which are volatilized. At  $256^{\circ}$  it becomes quite fluid, and, if kept long enough at that temperature, it loses all its water, and concretes into a reddish yellow resin. (Thomson, Ann. of Phil. xv.)

Resins dissolve in alcohol, ether, and essential oils; but not at all in water, which even precipitates them from the foregoing solvents. Of common resin, alcohol, sp. gr. 0.835, dissolves 1-8th of its weight at  $60^{\circ}$  Fahr.

Both acids and fixed alkalis act on resins; the pure alkalis most remarkably. The alkaline solution is clear, and may be diluted with water without decomposition; but acids immediately precipitate the resin. By mixing it with a solution of a metallic salt, the oxide is precipitated in combination with resin. Alkaline carbonates also dissolve resin when boiled along with it. The alkaline solutions have the properties of soap. Into common brown soap, indeed, a portion of resin always enters as an ingredient. Ammonia acts but feebly as a solvent of these bodies.

By long-continued and repeated digestion with nitric acid, the resins afford a deep yellow solution, which has the property of precipitating animal gelatine, and agrees, therefore, with tannin. No oxalic acid is obtained by this process, a circumstance which distinguishes the resins from all other vegetable substances. (Hatchett, Phil. Trans. 1805.)

Concentrated sulphuric acid dissolves the powdered resins. If the solution be digested in a moderate heat, sulphurous acid is first evolved; in a few days this ceases; and a black porous coal remains, equal to from 40 to 70 per cent. of the weight of the resin which has been employed; whereas, by incinerating resins in close vessels, little more than  $\frac{1}{100}$ th part their weight of coal is obtained. In the latter case, the charcoal is carried off in combination with hydrogen.

Acetic acid dissolves resins, which are precipitated from it by the addition of water.

Resins are the bases of varnishes, and are much used in medicine.

There is a remarkable want of agreement between different statements of the composition of the same kind of resin, arising, probably, from actual differences of the substance itself. Com-

mon resin afforded, in an analysis by Gay Lussac and Thenard,

Carbon ..	75.944	.... = 15 atoms	.... 90
Oxygen ..	13.337	.... = 2 do.	.... 16
Hydrogen	10.719	.... = 13 do.	.... 13
	<hr/>		<hr/>
	100.		119

But Dr. Thomson (Ann. of Phil. xv.), analyzing it by peroxide of copper, obtained

Carbon ..	63.15	.... = 10 atoms	.... 60
Oxygen ..	25.26	.... = 3 do.	.... 24
Hydrogen	11.59	.... = 11 do.	.... 11
	<hr/>		<hr/>
	100.		95

And resin which had been heated to 276°, and had lost a quantity of water, and probably of essential oil, afforded

Carbon ....	48.98	.... = 4 atoms	.... 24
Oxygen ....	48.98	.... = 3 do.	.... 24
Hydrogen ..	2.04	.... = 1 do.	.... 1
	<hr/>		<hr/>
	100.		49

Dr. Ure states the following as the results of his analysis of resin :

Carbon ....	75.00	.... = 8 atoms	.... 48
Oxygen ....	12.50	.... = 1 do.	.... 8
Hydrogen ..	12.50	.... = 8 do.	.... 8
	<hr/>		<hr/>
	100.		64

Statements, so much at variance with each other, show the necessity of a fresh appeal to experiment.

In the analysis of copal, also, there is some disagreement, though less considerable, between the results of MM. Gay Lussac and Thenard, and those of Dr. Ure. Copal consists, according to

	Carbon.	Oxygen.	Hydrogen.
Gay Lussac and Thenard ..	76.811	.. 10.606	.. 12.583
Dr. Ure, from experiment ..	75.	.. 12.50	.. 12.50
Ditto, from theory .....	80.30	.. 10.34	.. 9.36

In the theoretical view, the carbon is increased, on account of the difficulty which was experienced in burning copal completely by peroxide of copper. Thus modified, its constitution may be represented by 10 atoms of carbon + 1 of oxygen + 7 of hydrogen, and its equivalent by the number 75.



*Native balsams* are liquid resins, holding in combination a proportion of benzoic acid. (See 69 Ann. de Chim. 293.)

*Gum resins*, along with resin, have an admixture of extractive matter. They dissolve partly in water, and partly in alcohol. They are almost solely used in medicine. Asafœtida, gum-ammoniac, aloes, gamboge, myrrh, opium, &c., are varieties of gum-resin. The reader, who may wish for further information respecting the gum-resins, may consult Braconnot's Memoir in the 68th, and Pelletier's in the 80th, vol. of Annales de Chimie. In hepatic aloes, Tromsdorff found 12.5 per cent. of albumen.

*Guaiacum* was observed by Mr. Hatchett to differ from other resins in giving oxalic acid by the action of nitric acid, and very little tannin. In other respects, also, it has been since shown, by Mr. Brande, to possess properties that do not agree with those of resins in general. (Phil. Trans. 1806.)

*Amber* is a resin possessed of peculiar properties. It is found in some places beneath the surface of the earth, and in others on the sea-coast. It is hard, brittle, nearly transparent, sometimes almost colourless, but generally of a peculiar yellow colour, which has been called *amber yellow*. That it had originally a fluid form, is shown by its enclosing ants, the wings of insects, leaves, &c. Its sp. gr. is 1.065; it is insoluble in water. Alcohol, according to Berzelius, readily dissolves an odoriferous oil, and a yellow resin intimately united with this oil. But there is another resin in amber on which alcohol acts very little, unless when heated, and which is again deposited, as the liquid cools, in the form of a white powder, soluble in ether and alkalis. The solution of these two resins and of the oil in ether gives a viscid fluid which hardens in the air. Amber is soluble in boiling solution of potassa, and after a length of time in alkaline carbonates.

Weak acids do not act on amber. Sulphuric acid converts it into a black resinous mass. Nitric acid dissolves it, but no oxalic acid is formed. After being melted, it becomes soluble in linseed oil, and forms *amber varnish*.

By distillation *per se*, it yields a distinct acid, called the *succinic*, which has been obtained, also, from some varieties of turpentine, but it is not certain whether it exists in these substances ready formed, or is produced by the action of heat. The latter is the most probable view (see Ann. de Ch. et de Ph. xxx. 19), and is that also which is maintained by Berzelius, who finds

that the acid may be extracted, along with a peculiar balsam, from amber, by ether, alcohol, and alkalis. (Lib. cit. xxxviii. 220.)

To prepare succinic acid, let a glass retort be half filled with powdered amber, and the remainder with fine dry sand. Lute a receiver, and apply a gentle heat. A portion of water first comes over, which is succeeded by a weak acetic acid. The succinic acid then sublimes; but is contaminated by a mixture of oil. It may be purified by solution and crystallization; and it then forms transparent white shining crystals, having the form of triangular prisms. (See Colin and Robiquet, Ann. de Ch. et de Ph. iv. 326.) They are anhydrous, and require for solution nearly 100 times their weight of water; they dissolve also in boiling alcohol. The solution reddens the blue colour of turnsole, but not that of violets, and has an acid taste. It combines with alkalis, &c., and forms succinates, the most important of which is the succinate of ammonia. This salt decomposes all the per-salts of iron; and affords an insoluble precipitate, composed of succinate of iron. Hence it is highly useful in the analysis of mineral waters.

Berzelius (94 Ann. de Ch. 189) states the composition of the succinic acid as follows:

Hydrogen ..	4.512	.... = 2 atoms	....	2
Carbon ....	47.600	.... = 4 do.	....	24
Oxygen ....	47.888	.... = 3 do.	....	24
	100.			50

By experiments on its compound with peroxide of iron, Dr. Thomson, also, deduces 50 to be the equivalent of succinic acid. It is remarkable that the atomic weight of succinic acid not only agrees exactly with that of acetic acid, but that both acids are constituted of the same elements in the same proportions. Nor does this identity of composition impeach the accuracy of the analyses which have been made of these acids; since a difference of properties, it has been already shown by the example of the compounds of carbon and hydrogen, may arise from some other cause than difference of proportion, and may possibly depend on the peculiar mode in which the constituent atoms are grouped together.

*Succinate of potassa* crystallizes in three-sided prisms. It is bitter, very soluble, and deliquescent.

*Succinate of soda* forms beautiful transparent crystals, the form of which is described Ann. of Phil. vi. 236. They have a bitter taste, are not deliquescent, are less soluble than the foregoing salt, and are constituted of 1 atom of acid, 1 atom of base, and 6 atoms of water.

*Succinate of ammonia* does not readily crystallize, but may be obtained in small needles, which have a sharp, bitter taste, and may be sublimed without decomposition. Its solution precipitates peroxide of iron of a deep red colour. It also throws down baryta and mercury; and with the oxides of lead, copper, and perhaps some other oxides, forms white precipitates, which are dissolved on adding a large quantity of water. It is much employed as a test of iron.

*Succinate of baryta* is an almost insoluble compound.

*Succinate of strontia* forms crystals as fine as sand, which are considerably more soluble than the last-mentioned salt, and their solution precipitates barytic salts.

*Succinate of magnesia* is deliquescent and not crystallizable.

*Succinate of alumina* crystallizes in prisms.

*Succinate of manganese* forms rose-red crystals, insoluble in alcohol, and requiring 10 times their weight of water for solution.

*Succinate of iron*, formed by adding succinate of ammonia to the solution of any salt containing peroxide of iron, is insoluble in water. In 100 parts it contains 38.5 peroxide. To estimate the quantity of base, Dr. Thomson advises to multiply the weight of the precipitate, dried as perfectly as possible without decomposing it, by 0.444, which gives the peroxide of iron. To estimate the acid, multiply by 0.555. (Ann. of Phil. N. S. ii. 141.)

*Succinate of lead*, formed by double decomposition, consists, according to Berzelius, of 30.9 acid + 69.1 protoxide, or of 100 acid + 222 base. By digesting this compound in liquid ammonia, he obtained a sub-succinate consisting of 100 acid + 666 base. In the first salt we have an atom of each element; in the second 1 atom of acid + 3 atoms of base.

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## SECTION IX.

*Farina, Starch, or Fecula.*

Starch may be obtained from the flour of most varieties of grain, from the roots of the potato, and from almost every part of vegetables, by a very simple process. The grain, in the state of fine powder, or the root well rasped, is to be washed with a quantity of *cold* water, which becomes turbid; and, if the fecula is white, milky. The fecula, however, is not dissolved, but merely suspended mechanically; and, after separating the fibrous and grosser parts by a sieve, it subsides to the bottom of the vessel. The liquid, which contains the soluble parts of the vegetable, is to be decanted, and the farina to be washed by repeated affusions of cold water. It may afterwards be dried in a gentle heat.

When starch is prepared in the large way, grain is steeped in water till it becomes soft, and yields a milky fluid on pressure. It is then put into coarse sacks, which are strongly pressed in vats filled with water. The sacks are then removed, and the starch subsides to the bottom. Being suffered to remain some time, the supernatant fluid ferments, and acetous acid is formed, which dissolves the impurities, and leaves only the starch. On drying, the starch splits into columnar masses of a small size, forming prisms of considerable regularity. The process is fully described in the 29th vol. of the Philosophical Magazine.

MM. Raspail and Dumas have made some curious observations on the structure of starch, as discovered by the microscope. It appears to consist, not of crystals, but of small, round, hard, and translucent grains, exhibiting the appearance of fine beads of mother-of-pearl. Every grain is composed, 1st, of a smooth integument, not affected by acids at common temperatures, and susceptible of being coloured by iodine; 2dly, of a soluble substance, which, when heated, loses the character of being coloured by iodine, and acquires all the properties of gum. The diameter of the grains is not always the same, but differs in different varieties of fecula. These observations have been opposed by Caventou (*Ann. de Chim. et de Ph.* vols. xxxi. and xxxiii.), but they have been confirmed and extended by Guibourt. The latter has attentively examined the action of water and of iodine, both on the vesicles and their contents, before and after the action of hot water; and in starch

of various kinds, which, with Raspail, he finds consists of vesicles of various figures. (Id. xl. 183.)

From the analysis of Dr. Pearson\* we learn that 100 parts of the fresh potato root, deprived of skin, afford

Water .....	68 to 72
Meal .....	32 to 28
	100. 100.

The meal is composed of three distinct substances, *viz.*

Fecula .....	15 to 17
Fibrous matter .....	8 to 9
Extract or mucilage .....	5 to 6
	28 32

Some useful information respecting the quantity of starch in different varieties of the potato, and the methods of separating it, has been given by Mr. Skrimshire in the 21st vol. of Nicholson's Journal. In this root, according to Dr. Peschier, it is accompanied also by sugar. (Ann. of Phil. xii. 337.) The proportion of starch in sound and unsound grain, and the causes of unsoundness in corn and flour, have also been ably investigated by Mr. E. Davy, in a memoir published in the 49th volume of the Philosophical Magazine. Of rice, starch constitutes, according to Braconnot, from 83 to 85 per cent. (Ann. de Chim. et de Phys. iv. 383.) It may be extracted also from several substances which, from their properties, could scarcely be expected to contain it. M. Planche, for example, obtained from ginger a considerable quantity of starch, as pure and white as that from wheat. On the other hand, it has been shown that starch is not, as had been supposed, an ingredient of the emulsive seeds, such as almonds, which have been shown to contain albumen.

*Chemical Properties of Starch.*

Common starch, though not absolutely free from gluten, may be taken as a fair example of this substance. It will be found to have the following qualities:

\* Repertory of Arts, iii. 383. The analysis of several varieties of the potato by Lampadius may be seen in Thomson's Annals, v. 39.

It is not soluble in water, unless when heated to  $160^{\circ}$ ; and, if the temperature be raised to  $180^{\circ}$ , the solution coagulates into a thick tenacious transparent paste or jelly. By evaporation at a low heat, this paste shrinks, and at length forms a transparent brittle substance closely resembling gum, and, like it, soluble in cold water. Starch paste consists, therefore, in all probability, of modified starch, with a mixture of more or less of unaltered starch. With a minimum of starch, it is transparent or slightly opalescent; with a maximum of starch, it is opaque. In either of these states, when left exposed to the air, it becomes mouldy and sour, probably in consequence of the production of acetic acid. Caventou, however, is of opinion that the paste formed by treating starch with hot water is not a simple hydrate of starch, but that a greater change has taken place, indicated by the newly-acquired property of solubility in water. (Ann. de Ch. et de Ph. Apr. 1826.)

Starch is insoluble in alcohol and in ether. Pure liquid alkalis convert it into a transparent jelly. The alkaline compound is soluble in alcohol. It is decomposed by acids, and the starch is recovered.

Sulphuric acid dissolves starch slowly; sulphurous acid is evolved; and so much charcoal is disengaged, that the vessel may be inverted without spilling its contents. Diluted sulphuric acid has no solvent action on starch. Concentrated nitric acid, at the temperature of the atmosphere, acts on starch, and dissolves it; but no oxalic acid appears subsequently, unless the mixture be heated. Hot nitric acid is decomposed by starch, and oxalic acid is generated.

A solution of one part of starch in 90 parts of water is not affected by lime water, nor by strontitic water, but barytic water occasions a copious white flakey precipitate, which is redissolved by adding muriatic acid in excess. Silicated potassa effects no change in solution of starch. It is precipitated by sub-acetate of lead, but not by any other metallic salt.

Starch is dissolved by a hot infusion of nut-galls, but, as the solution cools, it becomes opaque, and deposits a curdy precipitate, which is again dissolved by a heat of  $120^{\circ}$  Fahr. and deposited again on cooling. This precipitate is composed of tan and starch, which seem capable of uniting in several proportions. Its alternate solution by a temperature of  $120^{\circ}$ , and

re-appearance on cooling, Dr. Thomson considers as characteristic of starch. (System of Chemistry, iv. 71.)

When starch and iodine are triturated together, both in a dry state, the starch assumes a violet tint, which passes to blue or to black, according to the proportions that are employed. The colour of this *ioduret*, or *iodide of starch*, is reddish, if the starch be in excess; it becomes a beautiful blue, when the two bodies are in due proportion; and black, when the iodine prevails. This compound is soluble in diluted sulphuric acid, and the liquor is of a fine blue colour. Concentrated sulphuric acid, also, dissolves it, and the solution is brown, but passes to a beautiful blue on the addition of water. There is also a *sub-iodide* of starch, which is white, but becomes blue by the action of almost any acid. (Colin and Gaultier de Claubry, 90 Ann. de Chim. 100.)

When four parts of starch, and one of finely powdered prussian blue, are intimately mixed, and then boiled in a considerable quantity of water, a liquid is obtained which, if heated with a solution of sulphate of iron, mixed with an equal volume of solution of chlorine, forms a very fine prussian blue. The starch, by this combination, appears to be changed in its nature, and converted into an imperfect kind of gum. (Ann. of Phil. xiii. 69.)

By the distillation of starch with peroxide of manganese and muriatic acid, an acid is evolved, which, when condensed and purified, appears to have peculiar properties. So little is known of it, that it is sufficient to refer to a short abstract of the memoir of its discoverer, M. Tünnerman, who has given it the name of *amylic acid*. (Quart. Journ. Dec. 1828.)

#### *Conversion of Starch into Sugar by Malting, &c.*

Starch, as it exists in grain, is spontaneously convertible into sugar. On this property is founded the process of malting.

The grain, from which malt is most commonly prepared, is barley. In this grain, Proust has discovered, beside the ingredients of wheat, a peculiar substance, nearly resembling sawdust in its external characters, to which he has given the name of *hordein*. (Ann. de Ch. et de Ph. v. 337.) This substance may be separated from starch by the action of hot water, in which it is quite insoluble. It has been analyzed by M. F. Marcet, and found to consist of

Carbon .....	44.2
Oxygen .....	47.6
Hydrogen .....	6.4
Azote .....	1.8

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100.

It differs, therefore, from starch, principally in containing a small quantity of nitrogen; and it is not improbable that this element may be traced to a minute proportion of gluten. During the process of malting, the proportion of hordein is considerably diminished, and it appears to be partly converted into sugar, or into starch, as will appear from the following comparative analysis of malted and unmalted barley :

	In 100 parts of barley.	In 100 parts of malt.
Resin .....	1	1
Gum .....	4	15
Sugar .....	5	15
Gluten .....	3	1
Starch .....	32	56
Hordein .....	55	12

It appears, then, that the formation of malt consists in the increase of gum, sugar, and starch, and the diminution of gluten and hordein. The starch, that remains after malting, is found changed in its properties; for it does not as before yield a viscid paste, capable of gelatinizing on cooling. The process of malting is not, however, essential to the production of alcohol from grain; for in the Scotch distilleries it has long been common to use a large proportion of unmalted barley; and M. Clément, by direct comparative experiments, obtained equal quantities of alcohol by fermenting the infusions of equal weights of malted and of unmalted grain. (Ann. de Chim. et de Phys. v. 422.) As, however, the proportion of crude grain is increased, the process appears to become more and more delicate, and the production of alcohol is more liable to be interrupted by the acetous fermentation. The practicability of converting starch at once into alcohol, without passing through the intermediate state of sugar, is proved also by the large proportion of alcohol which may be obtained by fermenting potatoes, 225 pounds of which yield about 34 pints of alcohol, sp. gr. 0.935. (Ann. de Chim. et de Phys. xiii. 288.) The



spirit obtained from unmalted barley has a peculiar odour, which is owing to its holding in solution a yellow solid oil, separable by careful distillation of the alcohol. (Thomson's Annals, xii. 35.)

The loss of weight sustained by grain in malting, which Proust states at one-third, Dr. Thomson asserts is greatly over-rated, and that it did not, on an average of 50 processes, carried on under his inspection upon a large scale, exceed one-fifth. The hordein of Proust, he considers as starch under some modification, which is changed, by malting, partly into true starch, and partly into sugar. (Ann. of Phil. x. 389.)

Another method of converting starch into sugar was discovered by M. Kirchoff of St. Petersburg. The change is effected by the action of diluted sulphuric acid, when boiled for many hours, with starch and water. The process has been successfully repeated by several persons, and among the rest by M. Vogel, (Ann. de Chim. l. 82,) and by Dr. Tuthill of London. (Nich. Journ. vol. 33.) The latter digested a pound and half of potato starch (obtained from  $8\frac{3}{4}$  pounds of potatoes), six pints of distilled water, and a quarter of an ounce by weight of sulphuric acid, in an earthen vessel, at a boiling heat; the mixture being frequently stirred, and kept at an uniform degree of fluidity by the supply of fresh water. In 24 hours there was an evident sweetness, which increased till the close of the process; at the end of 34 hours an ounce of finely powdered charcoal was added, and the boiling kept up two hours longer. The acid was then carefully saturated by recently burned lime; and the boiling continued for half an hour, after which the liquor was passed through calico, and the substance, remaining on the drainer, washed repeatedly with warm water. This, when dry, weighed seven-eighths of an ounce, and consisted of charcoal and sulphate of lime. The clear liquor, being evaporated to the consistence of syrup, and set aside, was in eight days converted into a crystalline mass, resembling common brown sugar, with a mixture of treacle. The saccharine matter, which Dr. Tuthill judged to be intermediate between cane sugar and grape sugar, weighed one pound and a quarter. By fermenting one pound of this substance in the usual manner, and distilling and rectifying the product, fourteen drachms by measure of proof spirit were obtained.

The differences between starch sugar and common sugar

from the sugar cane have been pointed out by Nasse. Starch sugar assumes the form of spherical crystals like honey. It is not so hard, nor so sweet, nor so soluble in water, as common sugar. When it is digested with an alkaline carbonate, a precipitation of mucilage takes place; and the same precipitation is occasioned from a solution of starch sugar by muriate of tin. The solution of starch sugar ferments without the addition of yeast, which is not the case with common sugar. (Thomson's Annals, vii. 47.)

It had been demonstrated, by Professor de la Rive of Geneva, that in the formation of sugar from starch no gas is evolved; that the alteration of the starch goes on in close vessels without the contact of air; and that no part of the sulphuric acid is either decomposed, or united to the starch as a constituent. These results were afterwards confirmed by the experiments of M. Theodore de Saussure, who has further shown that the sugar which is obtained exceeds by about one-tenth the original weight of the starch. (Thomson's Annals, vi. 424.) He concludes, therefore, that the conversion of starch into sugar is nothing else than the combination of starch with water in a solid state.

*Amyline.*—Starch, by being long kept in a state of mixture with water, either in vacuo or with the access of air, undergoes a series of changes which have been attentively investigated by Vogel and Saussure. Vogel found that starch and water, kept during four days in ebullition, became much more fluid, and that a liquid drained from it when placed on a linen cloth, which was mucilaginous and bitter, but not in the least degree saccharine. The residuum was insoluble in water, and resembled horn. Saussure left a paste formed of starch and 12 times its weight of water, exposed to the air with a wide surface during two years. (Phil. Trans. 1819.) It had then become a grey liquid, covered with mould, free from smell, and having no action on vegetable blue colours. The starch had lost nearly one-fourth of its weight, and the remainder was converted into the following substances:

1. Sugar, amounting to one-half of the starch;
2. Gum, or rather a substance resembling it, and analogous to what is obtained by roasting starch;
3. Amyline;
4. Starchy lignin;
5. Lignin mixed with charcoal.

Amyline (called *amydine* by Saussure) is intermediate

between gum and starch. It is soluble in boiling water, and the solution yields by evaporation a pale semitransparent yellow brittle substance, insoluble in alcohol, but soluble in ten times its weight of cold water, and to any amount in water at  $144^{\circ}$ . The solution is coagulated into a white paste by sub-acetate of lead. When treated with iodine, it assumes a blue colour. It is precipitated by barytic water, but not by fixed alkalis, nor by lime-water. By long boiling, it loses its property of becoming blue in iodine, which now renders it purple. Caventou differs from Saussure as to the origin of this modification of starch, and considers amyline not as the product of spontaneous decomposition, but as resulting from the temperature at which it is extracted from putrefied paste. (Ann. de Ch. et de Ph. xxxi. 342.) Guibourt accords with this view, and considers amyline as nothing more than modified starch. (xl. 193.)

*Starchy lignin.*—When the residue of the spontaneous decomposition of starch has been washed successively with cold and hot water, with alcohol, and with diluted sulphuric acid, an alkaline ley, containing  $\frac{1}{16}$ th its weight of potassa, still takes up a further portion. From this solution, diluted sulphuric acid precipitates a light brown combustible substance having the appearance of jet. It gives a blue colour to the aqueous solution of iodine, a property which, together with its solubility in a weak alkaline liquor, distinguishes it from common lignin. It is not impossible, however, that the effect of iodine may depend on the presence of a small quantity of starch.

*Effects of heat on starch.*—The starch of commerce, though apparently dry, was found by Dr. Prout to contain a considerable quantity of water. One hundred parts of a pure specimen, which had been kept in a dry situation for many months, lost, when subjected to a temperature between  $200^{\circ}$  and  $212^{\circ}$  for several hours, 12.5 parts. Even in this state, starch still appeared to retain water, a portion of which was separated by higher temperatures. Thus, after having been exposed as above for 24 hours to  $212^{\circ}$ , on being further submitted to a temperature between  $300^{\circ}$  and  $350^{\circ}$ , it lost 2.3 per cent. more. But, as it had acquired a slight yellow colour, and seemed to be altered in some of its properties, it had probably undergone some change of composition.

When more strongly heated, starch becomes first yellow, and afterwards assumes a reddish brown colour; it softens, swells,

and exhales a penetrating smell. If the process be stopped, a substance is the result, which is employed by calico-printers under the name of *British gum*. It is now entirely soluble in cold water; and its solution is not turned blue by iodine. This substance, however, Vauquelin finds is not a true mucilage; for with nitric acid it gives only oxalic acid, and no mucic acid.\* Lassaigue, by evaporating its aqueous solution to dryness, obtained a brownish yellow viscid matter. When boiling alcohol was digested with the dry mass, a fawn-coloured solution resulted, and this, by evaporation, gave a residuum which was only in part soluble by alcohol. The insoluble portion was taken up by water; and the solution, on evaporation, yielded a product very similar to the gum which exudes from some trees, at the period when they ripen their fruit. Even this gummy matter, however, gave only oxalic acid, without a trace of mucic or lactic acid, and differed therefore from true gum.

The experiments of M. F. Marcet, also, tend to show that torrefied starch is a distinct substance both from gum and from starch. (35 Ann. de Ch. et de Ph. 27.) When a few grains of the residuum of the watery solution are triturated in a mortar with an equal quantity of iodine, on adding a drop or two of water a fine purple colour is instantly developed, and dissolves in the water, if sufficient in quantity. (Caventou, 31 Ann. de Ch. et de Ph. Apr. 1826.) The same rich purple hue is produced by adding, to the watery solution of torrefied starch, a solution of iodine in water. The colour is destroyed by boiling water, by alcohol, by acids, and by alkalis; and, when thus destroyed by acids, it cannot be restored by alkalis, in this respect differing from iodide of starch. In chemical composition, also, starch undergoes by torrefaction a considerable change, as will presently be stated.

Starch, distilled in close vessels at a high temperature, yields an acid, which has been called the pyro-mucous, but which, in fact, is nothing more than vinegar holding an empyreumatic oil in solution.

*Analysis of starch.*—Starch has been analyzed, with different results, by Gay Lussac and Thenard, by Berzelius, by Dr.

\* 80 Ann. de Chim. 317. See also Annals of Phil. v. 38, xvi. 87; and Ann. de Chim. xc. 29.

Ure, and by Dr. Prout. Their discrepancies, it seems probable, have arisen from the different kinds and states of the starch submitted to experiment. Berzelius used potato starch; the rest starch of wheat. Dr. Prout analyzed it, both when of its ordinary dryness, and when desiccated by exposure for 20 hours to 200° or 212° Fahr.

*Table showing the Analyses of Starch.*

	Carbon.	Oxygen.	Hyd.
Gay Lussac and Thenard . . . . .	43.55	49.61	6.77
Berzelius (from potatos) . . . . .	43.481	48.455	7.064
Ure . . . . .	38.55	55.32	6.13
Prout (of ordinary dryness) . . . . .	37.5	55.76	6.74
Ditto (dried at 200 +) . . . . .	42.8	50.845	6.355
F. Marcet . . . . .	43.7	49.7	6.6
Ditto (torrefied) . . . . .	35.7	58.1	6.2

Considering the oxygen and hydrogen as forming water, Dr. Prout views the composition of starch as follows:

	Carbon.	Water.
Starch of ordinary dryness . . . . .	37.5	62.5
Desiccated at 200° . . . . .	42.8	57.2

Dr. Prout is, however, of opinion that differences of composition exist among the varieties of the amylaceous principle, analogous to those existing among sugars: in other words, that there are *low starches* as well as *low sugars*. Wheat starch he places at the head of the varieties of starch, and he considers arrow root as the lowest.

The *equivalent* of wheat starch, if deduced from its ultimate analysis, would approach very closely to that of pure cane sugar. It is probable, indeed, that in this, as well as in other instances of vegetable compounds, the difference between starch and sugar consists merely in the manner in which the elementary atoms are arranged; a view of the subject, with which the conversion of starch into sugar, by processes not attended with the evolution of any gaseous matter, is perfectly consistent. Berzelius investigated the equivalent of starch, by examining the composition of the insoluble *amylate of lead*, formed by mixing a boiling solution of potato starch with one of sub-nitrate of lead. (Ann. of Phil. v. 272.) This he found to consist of 72 parts of starch + 28 of pure oxide of lead; and, reasoning from its

composition, he infers that starch must be constituted, either of 6 atoms of oxygen + 7 of carbon + 13 of hydrogen, or of 18 atoms of oxygen + 21 of carbon + 39 of hydrogen. In this case, the same agreement does not exist between the number deducible from ultimate analysis and from a compound of the entire substance with oxide of lead, as in the instance of sugar; for the equivalent, most consistent with the first supposition, would be not less than 103; whereas that for sugar is only 81. In this, as in various other cases, where the constitution of organic substances is concerned, it is better to wait for the further progress of science, than to rest satisfied with equivalent numbers, which are not supported by the concurring results of different methods of investigation.

Beside the starch of the cerealia and of potatos, the following varieties of this substance are also met with.

*Indian arrow root* is obtained from the roots of the *Maranta Arundinacea*, L. a plant cultivated in the West Indies. The roots, first well-washed, are beaten in large and deep wooden mortars to a pulp. This is thrown into a tub full of clean water, where it is well worked with the hands, and the fibrous parts are wrung out and thrown away. The milky liquor is passed through a hair sieve and allowed to settle, and the clear liquor drained off. The powder at the bottom of the vessel is again repeatedly washed, and then dried in the sun. Caventou finds that arrow root agrees closely in chemical properties with potato starch. It yields only a very little gummy matter to cold water, but, like starch, is soluble by hot water. Dr. Prout submitted it to ultimate analysis, and found its constitution to approach as near as possible to that of sugar of honey, and also to that of wheat starch similarly exsiccated, *viz.* :

Carbon .....	42.8
Water .....	57.2

*Sago* is prepared from the pith of a palm-tree (*Cycas circinalis*, L.) which grows spontaneously in the East Indies. The pith is scooped out, diluted with water, and passed through a straining bag, which detains only the fibrous matter. The sago is allowed to settle, and when partly dry is granulated by forcing it through apertures of the proper size. Its colour is occasioned by the heat used in drying it. It is an uniform sub-

stance soluble in cold water, but more so in hot, precipitable blue by iodine, and differing from starch chiefly in its solubility in water at common temperatures. (Caventou.)

*Cassava and tapioca* are prepared from the roots of the *Jatropha Manihot*, a plant common in South America. By pressure, a juice of poisonous quality flows out; yet the sediment from it, called, when well washed and dried, *Cassava*, is perfectly innocent; and is made into a nutritious bread. *Tapioca* is the same substance, under a different form, which it assumes in drying. Both, according to Caventou, differ from starch, and are allied to sago.

*Salop*, or *saloop*, is the farina obtained from several species of *Orchis*, especially the *O. Masculata*. It is extracted by processes similar to those which have already been described. The experiments of Caventou have shown that it differs materially from ordinary starch, and that it consists partly of a gummy matter, soluble by cold water, and capable of passing through a filter, on which is left a gelatinous trembling mass, soluble in boiling water. This last consists of a very little gum and starch, and much *bassorine*. (31 Ann. de Ch. et de Ph. 345.)

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## SECTION X.

### *Gluten.*

Gluten may be obtained from wheat flour, by a very simple process. The flour is first to be formed, by the gradual addition of a small quantity of water, into a soft and ductile paste. This is to be washed by a very slender stream of water, and, at the same time, to be constantly worked between the fingers. The water carries off the starch, and for some time is rendered milky. When it passes off transparent, the washing may be discontinued; and the pure gluten remains in the hands.

The following are the properties of gluten :

It is of a grey colour, of a fibrous structure, and has so much elasticity, that when drawn out to several times its length, it recovers itself like elastic gum. It has scarcely any taste, and does not melt or lose its tenacity in the mouth.

When exposed to a gentle heat, it dries very slowly, and becomes hard, brittle, semi-transparent, of a dark brown colour,

and somewhat like glue. When broken it has the fracture of glass. In this state it is insoluble in water.

When kept moist, it ferments and undergoes a sort of putrefaction, emitting a very offensive odour. At the same time a portion of acid is developed, which is perceivable by its smell, and which considerably retards the putrefaction of the gluten. In this circumstance, chiefly, it differs from animal gluten or fibrin.

When suddenly heated, it first shrinks; then melts, blackens, and emits a smell like that of burning horn. By distillation in close vessels, it yields a portion of water impregnated with carbonate of ammonia; a considerable quantity of brown fetid thick oil; solid sub-carbonate of ammonia; and carbureted hydrogen gas. These products resemble, very closely, those of animal substances, especially in the large quantity of azote which they indicate as entering into its composition. It has not, however, been yet analyzed with a view to the proportions of its ultimate elements.

It is generally described to be insoluble in water, in alcohol, and in ether. After fermentation, it is partially soluble in alcohol, and the solution may be applied to the purposes of varnish. From the experiments of Dr. Bostock, gluten appears, however, by long digestion, to be partly soluble in water. The solution is precipitated by acetate and sub-acetate of lead, by muriate of tin, and by other re-agents. (Nich. Jour. xviii. 34.)

All acids dissolve gluten, and alkalis precipitate it, but considerably changed, and deprived of its elasticity. It undergoes a similar change when dissolved in pure alkalis, and precipitated by acids.

Gluten exists most abundantly in wheat-flour, of which it constitutes about one-fourth, and is essential to its soundness; but it is found, also, in various vegetable juices. (Proust in Nich. Journ. 8vo. iv. 273.) Sir H. Davy discovered a larger proportion of gluten in North American wheat, than in the wheat of this country; and in general found it more abundant in the wheat of warm climates. (El. of Agric. Chem. p. 141.) It is in consequence of its abounding in this principle, that the wheat of the South of Europe is peculiarly fitted for making macaroni and other glutinous preparations. The grain containing most gluten is distinguished by its hardness and great



specific gravity. Of particular grains, Sir H. Davy ascertained the composition of the following. He found

	Starch.	Gluten.
100 parts of good full-grained wheat } sown in Autumn to afford . . . . }	77 . . . .	19
100 parts of wheat sown in Spring . . . . .	70 . . . .	24
100 parts of Barbary wheat . . . . .	74 . . . .	23
100 parts of Sicilian wheat . . . . .	75 . . . .	21
100 parts of full and fair Norfolk barley	79 . . . .	6
100 parts of Suffolk rye . . . . .	6 . . . .	5

The above proportions exceed those resulting from the experiment of M. Henry of Paris, who obtained only  $10\frac{1}{4}$  per cent. of dry gluten from the flour of wheat, on an average of 25 or 30 samples of known purity, and from 6 to  $6\frac{1}{2}$  per cent. from adulterated flour. (Ann. de Chim. et de Ph. xl. 223.)

#### *Gliadine and Zimome.*

The experiments of M. Taddei, an Italian chemist, appeared to have proved that the gluten of wheat may be decomposed into two principles, one of which he distinguished by the name of *gliadine* (from  $\gamma\lambda\iota\alpha$ , gluten), the other of *zimome* (from  $\zeta\upsilon\mu\eta$ ,) a ferment. To separate them, he directs fresh gluten to be kneaded with repeated portions of alcohol, as long as that fluid becomes milky by dilution with water. The alcohol dissolves the gliadine and leaves the zimome. (Ann. of Phil. xv. 390; xvi. 88.)

Berzelius admits this elective property in alcohol, but contends that the new principles, which Taddei supposes he had discovered, are merely the well-known ones, gelatine and albumen. From the gluten, prepared by Beccaria's process, boiling alcohol, he finds, takes up a considerable portion, which separates on cooling. The spirituous solution being mixed with water and distilled, the aqueous liquid, left in the retort, deposits on cooling a coherent glutinous mass, similar to gluten. It is, in fact, vegetable gelatine, or gluten of the same nature as that extracted by Einhof from rye, barley, and peas, which do not yield a gluten like that of wheat. The matter insoluble in alcohol is so similar in appearance and chemical properties to animal albumen, that we cannot hesitate to consider it the same, and to designate it by the name *vegetable albumen*. When

precipitated from a weak solution by caustic alkali, it exactly resembles the white of egg. The emulsive seeds, the almond for instance, afford a precisely similar product.

From the alcoholic solution, vegetable jelly may be obtained solid, by gentle evaporation. It is then greyish, coherent, glutinous, and elastic, without taste, but having a peculiar odour. It gives a pale yellow colour to alcohol, and remains, after the evaporation of that liquid, in the form of a transparent varnish. It is almost entirely soluble in vinegar, and is precipitated unchanged by alkalis. With mineral acids in excess, it forms a glutinous compound, insoluble till the excess of acid is removed. It unites with caustic alkaline liquids, and, when it is in excess, covers their taste, so as to render it imperceptible. Ammonia and lime-water precipitate it from its acid solutions, and dissolve it anew. The persulphate of iron does not precipitate it from vinegar, but ferro-cyanate of potassa throws it down in a white semi-transparent mass. Its solutions in acids and in alkalis are decomposed also by bi-chloride of mercury, and by tincture of galls. Another striking analogy between this variety of gelatine, and that from animal sources, is that it combines with tan precisely like the latter. (*Ann. de Chim. et de Phys.* xxxvii. 215.)

M. Taddei afterwards discovered that powdered guaiacum is a test of the presence of that ingredient in flour, to which he gave the name of zimome, but which may now be regarded as identical with albumen. When good wheat flour is kneaded with water, and exposed to the air, the guaiacum assumes a very fine blue colour. Starch does not produce this colour, and bad flour only in a very small degree. But when guaiacum is worked up with pure zimome (albumen), the colour is instantly evolved, and is a superb blue. The contact of oxygen is necessary to this change. The powder of guaiacum, therefore, may be employed as a re-agent, to detect the change which flour sometimes undergoes by the destruction of its gluten, and to enable us to estimate in a general way the amount of its deterioration. (*Quart. Journ.* vii. 377.)

## SECTION XI.

*Caoutchouc, or Elastic Gum.*

Caoutchouc is chiefly the product of two trees, which are the growth of Brazil; the *Hoevea Caoutchouc* and *Jatropha Elastica*. When the bark of these trees is wounded, a white milky juice flows out, which speedily concretes in the air into an elastic substance; and, when the juice is applied in successive coats, upon clay moulds, it forms the globular bottles, which are brought to this country. By an immediate and careful seclusion from air, the juice may be preserved some time from concreting, and has occasionally been brought to Europe in a liquid state. But even when thus preserved, a part of it, in the course of time, passes to a solid form. Mr. Faraday has made it the subject of a set of experiments, described in the 21st. vol. of the Quarterly Journal. The fluid was pale yellow, thick, creamy-looking, and of uniform consistency. Its odour resembled that of putrescent milk. Its sp. gr. was 1011.74. Exposed to the air it solidified into caoutchouc of the usual quality; of which the sap contained in 100 parts, about 45, dried at 100 Fahr. The liquid was coagulated by heat, the caoutchouc separating and leaving an aqueous solution of the other substances existing in the native sap. Alcohol also partially coagulated it, leaving a solution of foreign matters in alcohol. Alkalis evolved a very fetid odour, but did not appear to affect the caoutchouc. The sap was purified from foreign substances, by dilution with four times its volume of water in a funnel. In 24 hours it rose to the top, and the water was drawn off at the bottom. In this way it was washed with solution of common salt, muriatic acid, and finally with pure water. It then appeared perfectly white, and was as capable of being solidified as before. The purified solid is, at first, soft, white, and opaque from interposed water, but becomes afterwards transparent, colourless, and elastic. Its sp. gr. is 0.925. It is a non-conductor of electricity.

Caoutchouc is inflammable, burning with a bright flame in atmospherical air, and with still greater brilliancy in oxygen gas, or in chlorine gas. It fuses at a heat which is not much below that required for melting lead. In this state Mr. A. Aikin finds that it may be brushed over iron or steel instru-

ments, and that it forms a transparent coating, which effectually preserves them from rust. The best method of melting it for this purpose is in a kind of copper flask, containing a horizontal stirrer or agitator, which is kept in motion by a handle rising above the flask. (Gill's Technical Repository, i. 54.)

It is insoluble in water and in alcohol. If long slips of caoutchouc, however, are tied spirally round a glass or metal rod, and boiled for an hour or two, the edges cohere, and a hollow tube is formed. It is soluble in ether; not, however, in the ordinary state of this fluid, as it is found in the shops. To render ether a fit solvent of this substance, it should be purified by washing it with water, in the manner to be hereafter described. The solution may be applied to the purpose of forming tubes or vessels of any shape. The principal difficulty in using it arises from the great volatility of the ether, in consequence of which the brushes, or other instruments, by which it is applied, are soon clogged up, and rendered useless.

Caoutchouc is soluble in volatile oils; but when they have evaporated, they leave it in a glutinous state, and deprived of much of its elasticity. In rectified native naphtha it swells to more than 30 times its bulk, becomes gelatinous and transparent, and finally dissolves, and also in the essential oil obtained by distilling coal tar. Petroleum dissolves it, and, when evaporated, leaves it unchanged. One of the most active solvents, however, of caoutchouc, appears to be the *cajeput oil*, a substance lately admitted into the Pharmacopœia of the London College of Physicians. A thick and glutinous solution is obtained, from which alcohol detaches the essential oil. The caoutchouc floats on the surface in a semi-fluid state, but soon hardens, and regains its elastic powers on exposure to the atmosphere.

The solubility of caoutchouc in coal naphtha renders it applicable to useful purposes. When interposed between two pieces of cloth, it renders the cloth completely water-proof, as in the patent process of Mr. Macintosh of Glasgow. One surface only of each piece is brushed over with the solution, and the besmeared surfaces being applied to each other, the pieces are united by passing between rollers. From the same solution, flat sheets of caoutchouc may be prepared, which may be applied to making flexible tubes, and to other uses in a laboratory. (See Faraday on Chem. Manip. § 416.)

Caoutchouc is acted on by alkalis; and, when steeped in them for some time, loses its elasticity.

The sulphuric acid is decomposed by it; sulphurous acid is disengaged; and charcoal remains. Nitric acid acts on it with the assistance of heat, nitrous gas is formed; and oxalic acid crystallizes from the residuum.

When distilled, it gives ammonia, and hence may be inferred to contain azote. A large quantity of olefiant gas and of very dense carbureted hydrogen, which burns with a remarkably bright flame, are at the same time evolved.

Caoutchouc, from the analysis of Dr. Ure (Phil. Trans. 1822), appears to consist of

Carbon	90.00	.....	3 atoms	....	18
Oxygen	0.88	.....	0 atom		
Hydrogen	9.12	.....	2 atoms	....	2
	100.				20

The experiments of Mr. Faraday agree with those of Dr. Ure in indicating carbon and hydrogen as the only elements of caoutchouc, but differ as to the proportions, which approach most nearly to 8 atoms of carbon and 7 atoms of hydrogen.

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## SECTION XII.

### *The Woody Fibre.—Lignin.*

AFTER removing all the soluble parts of wood, first by long boiling in successive portions of water, then by digestion in alcohol, and again by exposure to hot water, a fibrous substance is obtained, to which, by some chemists, the name of *Lignin* has been given. From whatever variety of wood it may have been procured, its properties appear to be uniformly the same.

It is perfectly destitute of taste, smell, and colour. In specific gravity, it is generally inferior to water. It is insoluble in water, at all temperatures.

The pure fixed alkalis act on the woody fibre, and render it soft, and of a brown colour. If equal weights of caustic potassa and sawings of wood are heated in a silver or iron crucible, stirring constantly, the wood softens and dissolves completely. Water poured upon the product when cold, dissolves the whole

of it, and the addition of an acid, in such quantity as barely to neutralize the alkali, precipitates a substance analogous to ulmin. (Ann. of Phil. xvi. 92.)

Concentrated sulphuric acid immediately blackens lignin, and, after sufficient digestion, converts it into charcoal. When dried sawings of hornbeam are mixed and agitated with sulphuric acid, and water is then added, a black powder falls; and the liquid, after being saturated with carbonate of lime and filtered, yields, by evaporation, a gum in several respects analogous to gum arabic. (Braconnot, Ann. of Phil. xvi. 90.)

Nitric acid decomposes lignin with the assistance of heat, and oxalic, malic, and acetic acids are formed.

When exposed to heat, lignin affords an acid called the *pyro-ligneous*, which has been proved to be identical with the acetic. (See the Chapter on Acetic Acid.) This acid holds in combination a quantity of essential oil, from which it may, by complicated processes, be entirely freed, and, also, a small proportion of ammonia. From the last mentioned product, it would appear that the woody fibre contains nitrogen. The pyro-ligneous acid in its crude state has been shown to be powerfully antiseptic, and advantageously applicable to the preservation of animal food. (Edin. Phil. Journ. iii. 21.) The charcoal, which remains in the retort, is greatly superior to that procured by the ordinary process; and hence distillation in iron cylinders has been, for some time past, practised as the best method of obtaining charcoal for the manufacture of gunpowder. Unlike coal and animal substances, all of which expand by carbonization, wood is contracted in volume by its conversion into charcoal.

By the distillation of wood on a large scale, Mr. P. Taylor, in 1812, obtained a peculiar inflammable and volatile fluid, resembling alcohol in some respects, but differing from it in others. (Quart. Journ. xiv. 436.) This fluid has been since more fully examined by MM. Macaire and Marcet, of Geneva. It is colourless and transparent. Its smell is strong, pungent, and ethereal, with a flavour of oil of peppermint; its taste is disagreeable. Its specific gravity, after being distilled from dry chloride of calcium, is 0.828. (0.812 Thomson.) It boils at 150° Fahr. When heated, it burns with a fine blue flame without leaving any residue. It contains a small portion of acetic acid, from which it may be freed by oxide of lead, and by recti-

fication. With water it forms an opalescent mixture resembling an emulsion, the component parts of which do not separate on standing. It is soluble in alcohol, but not in oil of turpentine. Camphor dissolves in it with great facility. It does not yield either olefiant gas or ether, when distilled with sulphuric acid; but nitric acid and chlorine convert it into a sort of ether, which has peculiar properties.

To this fluid MM. Macaire and Marcet have given the name of *pyroxilic spirit*, and have shown that it differs essentially from the pyro-acetic spirit described by Chenevix. By decomposition over ignited oxide of copper, it gave results indicating very nearly 6 atoms of carbon, 4 of oxygen, and 7 of hydrogen. (Ann. of Phil. N. S. viii. 69.)

The woody fibre, by exposure to the atmosphere in a perfectly dry state, does not undergo any change. The action of the air upon it, however, when moistened, causes it to pass through various shades of colour, into a black mould. If the process be carried on in a confined portion of oxygen gas, carbonic acid is formed. When excluded from the air, even moist wood shows very little tendency to decomposition.

It has been found by Prof. Autenreith, of Tubingen, that wood repeatedly boiled with water, then dried in an oven, and ground in the usual manner of corn, may be fermented with leaven, and made into palatable bread. (See Dr. Prout's Essay, Phil. Trans. 1827.)

Gay Lussac and Thenard have analyzed the wood of oak and beech, by combustion with chlorate of potassa, and Dr. Prout with peroxide of copper, by his new apparatus described Phil. Trans. 1827. In the experiments of the former, the wood was taken from the most compact part of a log, reduced to fine powder by a file; then sifted and washed in succession with water and alcohol; and finally dried, before its admixture with the chlorate.

	Carbon.	Oxygen.	Hydrogen.
100 parts of Oak contain	52.53	41.78	5.69
————— Beech ———	51.45	42.73	5.82

In both, the oxygen and hydrogen are in the proportions required to form water, and there is no excess of oxygen to acidify any part of the carbon. The atomic constitution of lignin, which agrees most nearly with the results of its ultimate analysis, is the following:

Carbon	.....	7 atoms	..	42	.....	53.86
Oxygen	.....	4 do.	..	32	.....	41.02
Hydrogen	....	4 do.	..	4	.....	5.12
					—	—
				78		100.

If deprived, therefore, of 1 atom of water and 3 atoms of carbon, the other elements of lignin should be convertible into acetic acid. Dr. Prout submitted the wood of box and willow, deprived of all soluble matter, and dried first at the temperature of the atmosphere, and afterwards by an oil bath at 300° or 350° Faht. In this state of desiccation it consisted of

		Box		Willow
Carbon	.....	50	.....	49.8
Water	.....	50	.....	50.2
		—		—
		100		100.

By the combustion of wood in open fires, a quantity of soot is collected in the chimney. This has been carefully analysed by Braconnot, and found to be of a very complicated nature, containing 15 different matters, one or two of which are new, and the remainder known salts, &c. (An. de Ch. et de Ph. xxxi. 55.)

### SECTION XIII.

#### *Colouring Matter.*

I. THE colouring matter of vegetables presents a considerable variety in its relation to chemical agents, depending partly on the diversity of the basis, or sub-stratum, in which it resides, and partly on intrinsic differences of the colouring matters themselves. Chaptal has arranged the varieties of the colouring principle under four heads. 1st, As it is attached to extractive matter: 2nd, As it resides in gum; in both which cases it is soluble in water: 3rd, As it exists in farina, or a substance analogous to it; and in this instance it dissolves most readily in sulphuric acid: 4th, The colouring principle is occasionally inherent in resin, and then it requires alcohol, an oil, or an alkali, for solution. But this arrangement must be considered as a temporary one, and must give place to one founded on better principles, as soon as our knowledge of colouring matter is more extensive and correct.



II. The extraction of colouring matter from the various substances that afford it, and its fixation on wool, silk, or cotton, constitute the art of DYEING; the details of which would be foreign to the purpose of this work. In this place I shall state only a few general principles; and refer for more minute information to a paper by Mr. Henry in the third volume of the *Manchester Memoirs*; to the works of Berthollet and Bancroft; and to a memoir of Thenard and Roard, in the 74th volume of *Annales de Chimie*.

Before attempting to fix colouring matter on cloth by the operations either of dyeing or printing, it is essential that the linen and cotton should first be completely cleared from every thing that can prevent the fixation of the colour, or the subsequent exhibition of its full effect. This is accomplished by the operation of BLEACHING, the general outline of which is extremely simple. The cloth is first steeped in warm water, to remove the *sowens* or weavers' dressing. It is next boiled or *bowked* with a solution of potassa, which is most economically applied in a caustic state, care being taken to use it so much diluted with water, as not to destroy the texture of the cloth. The goods, previously wetted with water, are laid in a large wooden vat or *bowking keir*, and the boiling alkaline ley is thrown, by a pump, over the surface of the goods, through which it penetrates, and, running out at the bottom, is returned to the pan and again heated. The cloth is then thoroughly washed, and is next steeped in a very weak solution of chloride of lime, or exposed on the grass, to the action of the light and air; then washed, and again bowked; and these operations are alternated as often as is necessary. It is next immersed in sulphuric acid, diluted with a large quantity of water to prevent it from injuring the texture of the cloth, and finally washed and dried. A pure white ground is thus obtained, on which the colours are afterwards displayed to the greatest advantage.

III. Of the various colouring substances, used in the art of dyeing, some are capable of being permanently attached to the dyed fabric, and fully communicating their colour to it, without the intervention of any other substance; while others leave a mere stain, removeable by washing with water. The latter class, however, may be durably attached by the mediation of what was formerly called a *mordant*, but has since been more properly termed, by the late Mr. Henry, a *basis*. The colours,

which are of themselves permanent, have been termed, by Dr. Bancroft, *substantive* colours; while those that require a basis, have been denominated *adjective* colours.

IV. The most important bases, by the mediation of which colouring matter is united with wool or cotton, are alumina, the oxide of iron, and the oxide of tin. Alumina and oxide of iron are applied in combination with sulphuric, or acetic acids; and the oxide of tin, united with nitro-muriatic, muriatic, acetic, or tartaric acids. From a comparison of the products of incinerating white calico with those of similar cloth dyed Turkey red, Dr. Ure found that the ashes obtained from the latter exceed in weight, by three times, those of the former. In 100 parts of the ashes of the dyed cloth,  $16\frac{2}{3}$  of alumina were discovered; while a scarcely perceptible trace of that earth could be detected in the ashes of white calico. (Quart. Jour. xxi. 28, 297.)

In dyeing, the most common method is to pass the substance to be dyed through a decoction of the colouring matter, and afterwards through a solution of the basis. The colouring principle thus becomes permanently fixed on the cloth, sometimes considerably changed by its union with the basis. In calico-printing, the basis, thickened with gum or flour paste, is applied to the cloth by wooden blocks, or copper cylinders. The cloth is then dried, and passed through a decoction of the colouring ingredient, which adheres only to that part of the cloth where the basis has been applied. From the rest of the cloth it may be removed by simple washing with water.

V. The variety of colours, observed in dyed substances, are reducible to four simple ones, *viz.* blue, red, yellow, and black.

1. Indigo is the only substance used in dyeing blue, which it does without the intervention of a basis. It is the production, chiefly, of several varieties of the plant called *Indigofera*, a native of America and of the East and West Indies. The plant, after being cut a little while before the time of flowering, is steeped with water in large vats, where it undergoes fermentation. During this process, a fine pulverulent pulp separates, which is at first green, but becomes blue by exposure to the atmosphere. The operations, by which indigo is separated and collected, are rather complicated, and cannot be described without considerable minuteness of detail. A good account of them may be seen in Messrs. Aikin's Chemical Dictionary. In this country, indigo has been extracted from the *isatis tinctoria*, or

*woad*, a plant of indigenous growth, by a fermentation, similar to that which is used when it is procured from the *indigofera*. Chevreul, also, by digesting woad in alcohol, and evaporating the solution, obtained white crystalline grains, which gradually became blue when exposed to the atmosphere. He considers them as indigo destitute of oxygen.

Indigo is a light friable substance of a deep blue colour, with sometimes a shade of violet or copper. The lightest as to weight is generally regarded as the best. It has been supposed to be a variety of starch or fecula, but it differs from that principle in several important particulars. Indigo is volatile, and may be in part sublimed at a temperature a little below that which is required for its decomposition.\* Water, by being boiled on it, dissolves only about a ninth or a twelfth the weight of the indigo. The colouring matter, however, remains untouched; and the solution, which appears to consist chiefly of extract, has a reddish brown hue. The indigo of commerce is never pure, but contains variable proportions of foreign matter, amounting generally to above half its weight. Bergman, in 100 parts of the best quality, found

Pure indigo .....	47
Gum .....	12
Resins .....	6
Earths .....	22
Oxide of iron .....	13
	100

The earthy matter consisted of baryta and lime in equal weights, with silica in the proportion of 1-10th of the whole earths.

Chevreul, by acting in succession upon Guatimala indigo, first with water, then with alcohol, and finally with muriatic acid, found its composition to be still more complicated. The yellow solution, obtained by hot water, let fall a greenish matter becoming blue on exposure to the air, and thus acquiring the properties of indigo. After this had ceased, green flocks formed and subsided, to which Chevreul gave the name of *green matter*. It is soluble in alkalis and alcohol, but is not convertible into indigo by exposure to air. From the indigo on which water had ceased to act, alcohol dissolved a further portion, the greater

\* Gay Lussac, 74 Ann. de Chim. 191.

part of which was the green matter, already described, with a *red matter*, differing only in colour, but possessing similar chemical characters. Lastly, muriatic acid dissolved more of the red matter, together with lime, alumina, and oxide of iron; and indigo, amounting to 45 parts from 100, and free from every thing but a little silica, remained.

Good indigo has a deep blue colour, inclining to purple, and is destitute both of taste and smell. Water has no immediate action upon it, but when long kept in a moist state, indigo is decomposed and emits a putrid smell. Alkaline solutions and lime water do not dissolve it, unless when fresh precipitated. In this state it is soluble also by carbonate of ammonia, but not by fixed alkaline carbonates. It is insoluble in alcohol, ether, and in fixed and volatile oils. Its appropriate, and indeed only, solvent, appears to be concentrated sulphuric acid. When thus dissolved, it is sometimes applied directly, in a diluted state, to various fabrics, and dyes what is termed a Saxon blue. But, by the abstraction of part of its oxygen, indigo becomes soluble in water; and its colour changes from blue to green. It recovers the former colour, however, on exposure to the air, by again absorbing oxygen, to the amount, Mr. Dalton finds, of 1-7th or 1-8th of the whole weight of the resulting indigo. Its de-oxidization is effected either by allowing it to ferment, along with bran or other vegetable matter; or by decomposing, in contact with it, the proto-sulphate of iron by the addition of lime. Substances dyed by indigo, thus deprived of oxygen, are green when taken out of the vat, and acquire a blue colour by exposure to the atmosphere. By this revival, the indigo again becomes insoluble, and fitted, therefore, for affording a permanent dye, not removeable by soap or by acids.

There appears, however, to be a certain stage of oxygenization in indigo, which is essential to the developement of its blue colour, and any proportion of oxygen either exceeding or falling short of this, is equally destructive of its perfect hue. Thus diluted nitric acid dissolves indigo, but the solution is yellow, and the indigo existing in it is decomposed. A thin layer of resinous matter appears, floating in the solution. If this be removed, and the solution, after evaporation to the consistence of honey, be re-dissolved in hot water, filtered, and mixed with a solution of potassa, yellow crystals appear, which consist of the bitter principle united with potassa. These crystals, being

wrapped in paper and struck with a hammer, detonate and emit a purple light. If to a drachm or two of finely powdered indigo we add an ounce measure of strong fuming nitrous acid, the mixture presently becomes hot, nitrous gas is evolved, a stream of sparks arises from it, and, finally, the whole bursts into flame. When the action of the nitric acid is moderated by adding an equal bulk of water, and the mixture, after being digested for some days, is evaporated to dryness, the residuum is soluble in water, and contains a small proportion of oxalic acid, with a considerable quantity of artificial tan. Benzoic acid may also be obtained from the dry mass by sublimation. It appears then that, by the action of nitric acid on indigo, there are generated oxalic and benzoic acids, tan, and the bitter principle. Muriatic, phosphoric, acetic, tartaric, and probably other acids, act on indigo only when it is fresh precipitated, and then they dissolve it and afford a blue liquid. Chlorine destroys its colour, and the same quantity of free chlorine discolours always the same quantity of pure indigo. Hence a solution of indigo in sulphuric acid has been employed for measuring the strength of solutions of chlorine and of chloride of lime, in order to regulate their application to the process of bleaching: and reciprocally a solution, containing a known quantity of chloride of lime, may be employed as a test of the strength or value of indigo. The use of this test, however, so as to insure accurate results, requires several precautions, which have been fully described by Mr. Dalton in the Manchester Society's Memoirs, vol. iv. N. S.

To obtain indigo of sufficient purity for accurate experiments, the yellow solution of indigo de-oxidized by three or four times its weight of proto-sulphate of iron, and about the same quantity of hydrate of lime, which forms the dyers' blue vat, may be agitated in contact with air, which will revive the indigo, and precipitate it purified to a certain degree. The precipitate may be digested in dilute muriatic acid, which will remove a little iron and carbonate of lime. It is then to be washed with distilled water, and dried.

Liebig digests 1.5 parts of indigo, 2 of proto-sulphate of iron, and 2.5 hydrate of lime with 50 or 60 parts of water, during 24 hours, the vessel, before introducing these materials, being filled with hydrogen gas. The liquid is drawn off by a syphon also filled with hydrogen gas, and is then mixed with muriatic acid diluted with water, in which a little sulphite of ammonia has

been dissolved. A thick white precipitate ensues, which immediately becomes blue by contact with air. It may, however, by particular management, be washed with solution of sulphite of ammonia, and even dried, without becoming blue. We have then a white substance, which Liebig considers as pure de-oxidated indigo, and to which he gives the name of *Indigogene*. It is insoluble in water and weak acids; combines with alkalis without neutralizing them; and is soluble in alcohol. It is not turned blue when dry, but, in a humid atmosphere or under water, assumes a blue colour. By a careful experiment, Liebig satisfied himself that indigogene, by being thus revived, acquires 11.5 per cent. of oxygen. With Berzelius he considers as untenable the theory of Doberëiner, who regards decoloured indigo, as a compound of indigo with hydrogen, to which he gives the name of *isatic acid*,—a compound entirely imaginary, and not necessary to explain the phenomena of the revival of indigo.

Indigo may be purified more completely by sublimation. About ten grains of purified indigo, in lumps of about one grain, may be placed in a shallow metallic capsule, of about three inches diameter, covered with a similar capsule, the concave sides of both being placed inwards, and at a distance not exceeding three eighths of an inch in the middle. Mr. Walter Crum, of Glasgow, who has published an ingenious paper on indigo in the *Ann. of Phil. N. S.* v. 81, used two platinum crucible covers; but similarly shaped vessels of other metals answer equally well. The lower capsule is to be heated by a spirit lamp; and when a hissing noise, which at first attends the process, has nearly ceased, the lamp is to be withdrawn, and the apparatus allowed to cool. On removing the cover, the sublimed indigo is found planted on its inner surface, forming long flat needles, in quantity equal to 18 or 20 per cent. of the original weight, and of a brilliant and intense copper colour. The colour, however, varies with the circumstances under which the crystals are observed. The specific gravity of the sublimate is 1.3.

Sublimed indigo is fusible and volatile at a heat of about 550° Fahr. leaving no residue when heated in open vessels. Its vapour is transparent and of a beautiful violet colour, differing from that of iodine by a shade of red. The melting point of indigo, that at which it sublimes, and that at which it is decomposed, appear to be remarkably near each other. Boiling oil of turpentine dissolves enough of purified indigo to acquire the

same fine violet colour as its vapour, but deposits it again on cooling.

By the ignition of sublimed indigo with peroxide of copper in green glass tubes, its analysis by Mr. Crum gave

Carbon .....	73.22
Azote .....	11.26
Oxygen .....	12.60
Hydrogen .....	2.92
	<hr/>
	100.00

These numbers correspond very nearly to

Carbon . . . .	16 atoms = 96	. . . . or . . . .	73.84
Azote . . . .	1 do. = 14	. . . . .	10.77
Oxygen . . . .	2 do. = 16	. . . . .	12.31
Hydrogen ..	4 do. = 4	. . . . .	3.08
	<hr/>		<hr/>
Equivalent number . . . .	130		100.

Mr. Dalton, adopting a number to represent the atom of nitrogen which is only one-half that commonly in use, assigns the following as the constitution of indigo.

Carbon .....	8 atoms = 48	. . . . or . . . .	75.5
Azote .....	1 do. = 7	. . . . .	7.7
Oxygen .....	1 do. = 8	. . . . .	12.3
Hydrogen . . . .	2 do. = 2	. . . . .	3.5
	<hr/>		<hr/>
	65		100.

When indigo is acted upon by strong sulphuric acid, it is not merely dissolved, but, if heat be applied, is, in less than 25 hours, changed into a new substance. Its colour first becomes yellow, owing, Mr. Crum believes, to the acid depriving the indigo of its oxygen and hydrogen; for great heat takes place, and the original blue colour is instantly restored on the addition of water. No sulphurous acid is evolved, nor is there any absorption of oxygen from the air, or any separation of carbon. From the solution, diluted with water, potassa and its sulphate throw down a deep blue precipitate, which is soluble in water, and capable of passing through a filter, but is not soluble in saturated solutions of salts with base of potassa. The precipitate was purified, therefore, by washing, first with a solution of acetate of potassa, and then with alcohol. The edulcorated precipitate has, when wet, a colour of so deep a blue; as to appear black; when dry it is copper-red. It attracts water rapidly from the air; is

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soluble to a considerable extent in boiling water; but requires 140 parts of cold water for solution. Water containing only  $\frac{1}{500}$  of its weight of the precipitate is still distinctly blue. The cold solution, diluted with 20 parts of water, is precipitated by salts of potassa, soda, lime, baryta, strontia, lead, and mercury, and the precipitates are not redissolved by acids. A variety of other salts that were tried were found not to produce the same effect.

From the analysis of this precipitate, Mr. Crum considers it to be a compound of sulphate of potassa with a peculiar substance, to which he gives the name of *Cerulin*, and to the precipitate that of *Ceruleo-sulphate of potassa*. In its property of forming insoluble compounds with neutral salts, cerulin is analogous to *tan*, which, according to Sir H. Davy, has similar effects on several of the salts of potassa. From its ultimate analysis, cerulin appeared to consist of 1 atom of indigo + 4 atoms of water.

If the action of the sulphuric acid on indigo be suspended, before it has gone far enough to produce *cerulin*, which, at the ordinary heat of summer, may be three hours, (at 100 Fahr., twenty minutes) a new substance, altogether different from cerulin, is produced, possessing rather singular properties. One part of purified indigo may be agitated with ten of sulphuric acid in a stoppered vial, till it assumes a bottle-green colour, then poured into a large quantity of distilled water, agitated, and thrown on a filter. On continuing to wash the substance on the filter, with more water, the first washings are colourless, and must be thrown away; but afterwards a blue liquid passes through, which contains the new substance. Muriate of potassa precipitates it of a beautiful reddish purple colour, exactly similar to that of the vapour of indigo. The precipitate is to be thrown on a filter, and washed with distilled water, till the liquid, which passes through, forms a red precipitate with nitrate of silver. Or, if the solution of indigo in sulphuric acid be kept till it has lost its yellow colour and become blue, which happens in a few hours, the addition of water precipitates a purple substance quite different from indigo. From the property, possessed by this substance, of becoming purple-coloured on the addition of certain salts, Mr. Crum terms it *phenecin*.

Phenecin is soluble both in water and alcohol, and the solution in both cases is blue. All saline substances without exception precipitate it again of its original colour, but some require to be



added in much larger proportion than others. Acids do not prevent its precipitation. It dissolves in liquid ammonia, but fixed alkalis destroy it, though not very easily. Sulphuric acid dissolves it, and in due time converts it wholly into cerulin.

From its ultimate analysis, Mr. Crum is disposed to consider phenecin as constituted of 1 indigo + 2 water. In the formation of this substance, therefore, as well as of cerulin, indigo appears to combine with water; but whether the sulphuric acid is actually robbed of a portion of water, or merely prepares the substance for combining with water afterwards, remains to be determined by further experiments.

*New Experiments on Indigo by Berzelius.*

An elaborate memoir on Indigo has been published by Berzelius in the *Ann. de Ch. et de Phys.* for Nov. and Dec. 1827. Of this I am induced to give a fuller abstract than would have been required for the use of the general reader, by the great importance of indigo in the arts of dyeing and calico-printing.

Berzelius finds in indigo four peculiar substances which constitute its chief ingredients, *viz.* 1st, a matter analogous to gluten; 2d, a brown matter; 3d, a red matter, (resin of Bergman and Chevreul); 4th, the proper blue colouring matter of indigo.

Gluten is extracted by steeping ground indigo with any weak acid, and then subjecting it, thrice successively, to the action of boiling water. Any excess of acid in the liquid is neutralized by marble, and the liquid is filtered and evaporated. From the dry mass, alcohol extracts a substance, which, though not perfectly identical with gluten, possesses the properties of that substance rather than of any other.

The residuum, left by the acid, is next gently heated with weak solution of caustic potassa. From the strained liquid, acids throw down a gelatinous bulky mass. Any excess of acid that may be present must be removed by marble, and the remainder digested with alcohol, which takes up a further portion of gluten. What remains is the *brown matter*, probably, however, not perfectly insulated. It has scarcely any taste; has neither acid nor alkaline re-action; burns with the same odour as animal substances; forms with acids insoluble compounds, and with alkalis soluble ones of a deep brown colour. Its compounds with lime and baryta are, however, insoluble. It is distinguished

from vegetable albumen and gelatine, inasmuch as its solution in vinegar is not precipitated by tan, corrosive sublimate, or ferro-cyanate of potassa. It is most probably the green matter of Chevreul, which product, as obtained by him, was rendered green by a combination of brown matter with unaltered indigo.

The *red matter* is extracted from the residuum left by alkalis, by repeated boilings with alcohol, sp. gr. 0.830. This solution contains also some brown matter in union with alkali. Adding vinegar in excess, the brown matter remains dissolved, and the red matter is precipitated; and being again dissolved by alcohol gives a fine red solution. By evaporation at a gentle heat, it is obtained dry.

The *red matter* is insoluble in water, dilute acids, and caustic alkaline liquids; sparingly soluble in alcohol, but abundantly in ether. These two last solutions, being evaporated, leave a powder of a deep red colour, soluble in concentrated sulphuric acid, and giving a deep yellow liquor. The action of heat upon the red powder, is very remarkable. In contact with air it burns with flame and a dense smoke; but in close vessels, it yields a solid crystalline sublimate destitute of colour, and, by digestion with alcohol and resublimation, rendered as white as snow. Nitric acid reconverts this sublimate into red matter.

*Pure indigo.*—The residue left by alcohol is not pure indigo. Beside insoluble impurities, it contains a portion of the green, brown, and red matters. It is necessary now to act upon it with lime and proto-sulphate of iron. Muriatic acid, added to the solution, retains some of the impurities; while the revived indigo falls down, and may be purified by washing with water. Even yet, it is not entirely free from a minute portion of red matter.

Indigo thus revived being again dissolved as before, and acetic acid added out of contact with air, a precipitate falls. This, after being well washed, and dried between folds of blotting paper, is greyish-white, with a kind of silky lustre, without smell, and without effect as a re-agent. It is totally insoluble in water, but soluble in alcohol and ether, to which it gives a yellow colour. Agitated in water which has not been purged of air, it instantly becomes blue, but assumes that colour very slowly when dry. In weak acids it is insoluble, but instantly dissolves in concentrated sulphuric acid, which it renders first purple and then blue. In alkalis, both caustic and mild, it dissolves readily. Lime affords by union with it two

compounds, the one, saturated with indigo, soluble; the other, with excess of base, insoluble. In general, these combinations become more rapidly blue than revived indigo itself. (Ann. de Ch. et de Ph. xxxv. 269.)

The action of sulphuric acid on revived indigo, Berzelius remarks, is attended with a decomposition, more or less complete, of the acid. Hypo-sulphuric acid (vol. 1. p. 419), he finds, is formed, which acid has the property of uniting with organic matters, the latter acting as bases, and forming permanent compounds.

Fuming sulphuric acid dissolves revived indigo rapidly, and without the disengagement of any sulphurous acid. Six parts by weight are sufficient for one of indigo; but of the common acid, one half more is required. The solution contains a compound of indigo with sulphuric acid,—another of indigo with hypo-sulphuric acid,—and a third of indigo with sulphuric acid in a peculiar state, which may be called *purple of indigo* (*pourpre d'indigo*). Probably the hypo-sulphuric acid may have been formed by the decomposition of a portion of indigo, which, at the same time, has given origin to the new purple substance. The more fuming the sulphuric acid, the greater is the quantity of hyposulphuric acid produced. The one compound Berzelius calls *blue sulphuric acid*, the other *blue hypo-sulphuric acid*, and their compounds with bases *blue sulphates* and *blue hypo-sulphates*.

When the solution of indigo in sulphuric acid is diluted with from 30 to 50 times its weight of water, the purple of indigo may be separated by a filter, on which it remains. From the filtered liquid, gently heated, well cleansed flannel or wool absorbs the two blue acids, leaving the excess of sulphuric acid and the other impurities. Water containing a little ammonia extracts the two coloured acids from the flannel. The liquid is evaporated to dryness at a temperature of 140° Fahr. Alcohol sp. gr. .830 extracts the blue hypo-sulphate of ammonia, and leaves untouched the blue sulphate of the same base. The latter is decomposed by dissolving in water, and adding acetate of lead. This gives a precipitate of blue sulphate of indigo, which is to be thrown on a filter. The liquid that passes is generally coloured by a little purple of indigo. The salt of lead is first well washed, then diffused in water, and decomposed by sulphureted hydrogen, from whence results a liquid at first

yellow, but becoming blue in the air. Evaporating it to dryness at a temperature not exceeding  $140^{\circ}$  Fahr., we obtain the blue sulphuric acid. It deliquesces, gives a fine blue colour to water, dissolves in water, and has an acid astringent taste.

The blue hyposulphuric acid is obtained by mixing the alcoholic solution with a solution of acetate of lead in alcohol, and treating the blue precipitate like the foregoing.

These two blue acids constitute what has been considered as one, under the name of *sulphate of indigo*. They both appear to form with wool compounds analogous to those which they compose with bases; but they do not quit those bases to unite with wool, unless an acid, however weak, vinegar for instance, co-operates.

The blue sulphates and blue hypo-sulphates are best produced by the direct combination of those acids with bases. Two salts, formed by these acids with a given base, differ essentially from each other; the blue sulphates, for instance, are not soluble in alcohol or water, which fluids readily dissolve the analogous hyposulphates.

The purple of indigo is constantly produced, when we treat indigo with sulphuric acid, and after some hours dilute the liquid with forty parts of water. If Nordhausen acid be employed, the dilution must be made immediately after solution. The purple matter appears to be indigo in a state intermediate between its ordinary and its soluble states. It is not dissolved by dilute acids, and may be collected on a filter; but it is sparingly dissolved by water. It was first discovered by Mr. Crum, who has described it under the name of *phenecin*.

#### *Action of Nitric Acid on Indigo.*

By acting, with nitric acid, upon indigo, Haussmann, so long ago as 1788, first obtained a bitter substance, which was successively examined by Fourcroy and Vauquelin, and by Chevreul, and more recently by Liebig. (Ann. de Ch. et de Ph. xxxv.) According to the last mentioned chemist, eight parts of the best East India indigo of first quality, coarsely powdered, are to be treated with eight or ten times its weight of nitric acid of mean strength, at a moderate heat. The indigo dissolves with a considerable disengagement of nitrous acid vapours, and swelling of the mass. The froth having subsided, the liquid is to be boiled, and concentrated nitric acid added till the red fumes

cease to be disengaged. After the cooling, a great quantity of yellow semitransparent crystals appear, and, if the process has been successfully performed, without resin or artificial tan. The crystals are washed with cold water, and boiled in water sufficient for their solution. If a few drops of tan should appear on the surface, they are to be removed by blotting paper. The filtered liquid deposits foliated, yellow, brilliant crystals, which lose nothing of their lustre by being washed with water. Being dissolved in water, and neutralized with carbonate of potassa, a salt is formed which is to be purified by repeated crystallizations. On mixing the first mother liquor with water, a copious brown precipitate appears, which, being washed and dissolved in boiling water, and then neutralized by carbonate of potassa, gives a considerable product of the same salt. To the whole of the purified salt of potassa, re-dissolved in boiling water, nitric, muriatic, or sulphuric acid is to be added; and, on cooling, very brilliant foliated crystals are formed of a clear yellow, which have mostly the form of equilateral triangles.

Dissolved in water, these crystals redden turnsole; they have an exceedingly bitter taste; act with considerable energy upon metallic oxides, which they neutralize, and form crystallizable salts. When heated on a silver spoon, they fuse, and are volatilized without decomposition; in a stronger heat suddenly applied, they take fire without explosion, producing a yellow flame, and leaving a residuum of charcoal. They dissolve in cold water, but more abundantly in hot, and the solution has a colour more intense than the solid. Ether and alcohol dissolve them readily.

Neither chlorine nor iodine acts upon the fused crystals. Concentrated sulphuric acid does not dissolve them unless when heated; and they are afterwards precipitated unchanged by water. Boiling muriatic, and nitro-muriatic acids, have no action.

The crystallized substance contains no nitric acid, and no oxalic or other organic acid. Mixed with oxide of copper, and heated to redness in a tube of glass, a mixture of gases is evolved, in which analysis, taking a mean of five experiments, were discovered 20 vols. of azote and 100 of carbonic acid, giving for the constitution of the substance,

Carbon .....	31.457
Azote .....	14.766
Oxygen .....	53.777

---

100.

Water is also formed by distilling the crystals with peroxide of copper, but in such very minute quantity, that we cannot consider that fluid, or even its element, hydrogen, to be essential to the composition of the crystals. The disengaged gases were entirely free from oxide of carbon, and from the oxides of azote.

The bitter principle (*amer*) of Welter, formed by acting in a similar manner with nitric acid upon silk, furnishes the same product, but in less quantity than indigo. Liebig has proved, also, that the action of nitric acid on aloes developes an acid identical with the foregoing. (An. de Ch. et de Ph. xxxvii. 171.)

As this substance appears to be a peculiar acid, Liebig has given it the name of *Carbazotic Acid*. With alkalis, earths, and metallic oxides, it composes a distinct genus of salts, to which he gives the appellation of *Carbazotates*. Several of these (those of potassa, baryta, lime, magnesia) detonate violently when heated; but the carbazotates with base of metallic oxides easily abandon their oxygen, and do not detonate by heat.

*Acid of indigo*.—Chevreul was the first who recognized, in the products of indigo acted upon by nitric acid, a new acid to which he gave this appellation; but the process, as conducted by him, did not afford it in a state of purity. Liebig has since examined it, and has been followed by Buff. (An. de Ch. et Ph. xxxvii. 160.) To obtain it, the nitric acid must be more largely diluted, and kept so during the additions of powdered indigo, by occasionally adding a little hot water. This prevents the formation of carbazotic acid; but the new acid is still mingled with resinous matter, from which it may be partly purified, by combining it with oxide of lead, then disengaging it by sulphuric acid; and afterwards combining it with baryta, from which it may be detached by an equivalent quantity of sulphuric acid. It has then the form of needles of a silky whiteness, and gives a colourless solution; it dissolves in 1000 times its weight of water; its taste is a mixture of sour and bitter. It may be sublimed unaltered by heating it in a glass tube; in the open

air it burns easily with a flame, which deposits much smoke. Concentrated nitric acid changes it into carbazotic acid. It is capable of forming with gases neutral salts, which are decomposed by heat without exploding.

The analysis of this substance with peroxide of copper gave the following proportion of its elements :

Hydrogen .....	2.417
Azote .....	7.225
Carbon .....	46.244
Oxygen .....	44.144
	100.

*Red dyes.*—The substances chiefly employed for affording *red colours*, are cochineal (an insect which has been supposed to derive colour from its food, the leaves of the *cactus opuntia*, L.) archil, madder, brazil-wood, and safflower. The first four are soluble in water; the last not without the intervention of an alkali. They are all adjective colours. Cochineal, though its colour is naturally crimson, is used for dyeing scarlet; and to evolve the scarlet hue, it is necessary to employ the super-tartrate of potassa. The basis, by which it is attached to cloth, is the oxide of tin. This may be exhibited by an easy experiment. A decoction of cochineal will leave only a fugitive stain on a piece of cloth; but if, in the decoction, some supertartrate of potassa has been dissolved, and a portion of nitro-muriate of tin afterwards been added, it will impart a permanent scarlet colour.

*Madder* has been lately subjected to a very attentive analysis by Colin and Robiquet. (An. de Ch. et de Ph. xxxiv. 225.) They digested ground madder, during ten minutes, with thrice its weight of water, and threw the mass on a filter, subjecting it afterwards to pressure. A reddish brown liquid was obtained, which had an acid re-agency; was coagulated by acids, which produced fawn-coloured flocks; but a few drops of liquid potassa rendered it again limpid, and gave it a fine red tint. A portion of the expressed liquor, being set apart, coagulated like blood into clots, from which oozed a fluid, less coloured than the rest. The coagulum, first drained, was deprived of water by pressure, very carefully applied to it between folds of cloth. It was then dissolved by alcohol, of which four-fifths were distilled off, and to the remainder a little sulphuric acid was

added, and afterwards much water. An abundant fawn-coloured precipitate was formed, which was washed with distilled water till it ceased to affect barytic solutions.

This substance, being heated in a tube, gave a sublimate of long, fine, and brilliant crystals, in colour resembling native chromate of lead. They were sparingly soluble in water; soluble in boiling water, to which they imparted a rose red tint; and soluble in alcohol and ether. The action of fixed alkalis is not uniformly the same, but to solution of ammonia they impart a splendid colour.

To another portion of the fawn-coloured precipitate they added ether, and obtained the same substance in the form of gold yellow micaceous plates, resembling *aurum musivum*. By whichever of these processes obtained, they consider the substance as identically the same, and propose for it the name of *alixarine*, derived from the commercial term *ali-zari*, applied in the Levant to madder-root. This principle they apprehend to be the real colouring ingredient of madder, if one only exist; or a part, if compounded. Its complete identity, however, with the colouring principle of madder, does not appear to be yet established beyond dispute. Zenneck has somewhat modified the process for obtaining this new principle, which he finds to be more easily extracted from madder, which, after being washed with water, has been fermented with the addition of yeast. He finds that it possesses decidedly acid properties; that a pound of boiling water dissolves only one grain, 210 of alcohol and 160 of ether at common temperatures take up one grain; it combines with alkalis; oxidates, and dissolves metals; and passes to the positive pole of the Voltaic pile. (Quart. Journ., March 1829, p. 198.)

The *yellow dyes* are wild American hiccory, sumach, turmeric, fustic, and quercitron bark; which afford various colours, accordingly as they are combined with the cloth, by the intervention of alumina, or of oxide of iron, or tin. Thus, with the aluminous base, the quercitron bark yields a bright yellow; with oxide of tin, all the shades, from pale lemon colour to a deep orange; and with oxide of iron, a drab colour. With the addition of indigo, it gives a green.

A combination of red oxide of iron, with the gallic acid and tan, is the principal *black colour*, which has therefore the same basis as common writing ink. In calico-printing, white spots,



or figures, on a black ground, are produced, by previously printing on the cloth a protecting paste of citric acid, thickened with gum or flour. The parts to which this paste is applied do not receive the black dye, but remain perfectly white.

VI. The colouring matter of vegetables, besides being capable of fixation on cloth, may be obtained in a dry form, in combination with a base only. Thus, if to a decoction or infusion of madder in water, a solution of sulphate of alumina be added, the colouring matter is precipitated in combination with the alumina, forming what is termed a *lake*. For obtaining this, the following process is given by Sir H. Englefield. Put two ounces of Dutch crop-madder into a calico bag, capable of holding three or four times that quantity. Pour on it a pint of distilled water, and triturate in a mortar, as much as can be done, without destroying the bag. The water becomes loaded with colouring matter, and is opaque and muddy. Pour off this portion, and repeat the operation till no more colour is obtained, which will generally happen after the fifth or sixth affusion. Pour these several washings into an earthen or well-tinned copper pan; and apply heat till the liquor boils. Let it then be poured into a basin; and one ounce of alum, dissolved in a pint of water, be added, and mixing by stirring. Add an ounce and a half of saturated solution of sub-carbonate of potassa; a violent effervescence will ensue, and the colouring matter will be precipitated. Stir the mixture till cold, and wash repeatedly with boiling water. About half an ounce of lake will be obtained, containing two-fifths its weight of alumina.

Other lakes may be obtained, of different colours, by the substitution of different dyeing woods; and from the infusion of cochineal (an insect of which there are several species), the beautiful pigment called *Carmin* is precipitated by means of a solution of tin. In 100 parts of cochineal, Dr. John found 50 cochineal (colouring matter), 10.5 gelatine, 10 waxy fat, 14 modified gelatinous mucus, 14 membrane, 1.5 saline matters. Pelletier and Caventou have also added to our knowledge of cochineal. (Journ. de Pharm. iv. 193.)

## SECTION XIV.

*Tan, Tannin, or the Tanning Principle.*

Tan exists abundantly in the bark of the oak, the willow, in some varieties of cinchona, mimosa, &c. and in the seeds of grapes. In barks, the layers next to the wood contain the largest proportion; the middle and coloured part, the next; and in this it is accompanied with more extract; the epidermis affords very little. The quantity is greatest at the time the buds begin to open, and is smallest in winter, and after a cold spring. It occurs also along with gallic acid and extract, in the several varieties of tea, but in variable proportions, (Quart. Journ. xii. 201;) it forms about one-half of the substance known in pharmacy by the names of terra japonica, or catechu, and exists, united with extractive matter, in kino, rhatania, &c.

The infusion of gall-nuts in water has been long known to be a source of tan, but not in a state of purity. Along with pure tan, Berzelius finds a little gallic acid; tannates and gallates of potash and lime; modified tan in the state most nearly approaching to extract; and, lastly, a combination, insoluble in cold water, of tan with some other substance, probably pectic acid. (An. de Ch. et de Ph. xxxvii. 385.)

*Processes for preparing Tan.*

The best re-agents for preparing tan from galls are the sulphuric acid and potash.

Tan may be obtained pure, according to Berzelius, by means of sulphuric acid, in the following manner. To a hot infusion of the gall-nut, add a very small quantity of weak sulphuric acid, and mix them completely. A thin coagulum appears, which contains tan and extract; and which, as in the clarification of liquids by white of egg, envelops the body in suspension, so that the liquid part admits of being separated by filtering. To the filtered liquid add sulphuric acid, diluted with half its weight of water, and agitate the precipitate which will be formed. In doing this, pour in the acid by a little at once, till the precipitate is seen, after half an hour's rest, to become a semi-fluid glutinous mass. As soon as this change of its nature is apparent, decant the liquid, and carefully add concentrated sulphuric acid, till no more precipitation ensues. We then obtain a

white mass verging towards yellow, which is a compound of sulphuric acid and tan, and which is insoluble in weak acids. Place it on a filter, and wash it with water mixed with much sulphuric acid; then press it between folds of unsized paper, and dissolve it in pure water, with which it forms a pale yellow solution. Add, in small portions, finely powdered carbonate of lead, which saturates the excess of sulphuric acid, and, after a short maceration, saturates also that which was combined with the tan. As soon as this saturation has taken place, the colour passes to deep yellow. Filter the liquid, and evaporate to dryness, which is best done in a vacuum. We now obtain a hard mass of a brownish yellow colour, which consists of tan mixed with extract formed by contact with the air. This mass, being pulverized, is digested with ether, till it ceases to act as a solvent. The ether is allowed to evaporate spontaneously, and the pure tan remains under the form of a transparent mass, scarcely yellowish, and unalterable in the air. What is left by the ether is the brown extract, which is not entirely soluble in water.

Berzelius describes also the following improvements on the process for obtaining tan by alkalis:—Mix a filtered infusion of nut-galls with a concentrated solution of carbonate of potassa, so long as a white precipitate appears, but no longer, because an excess of alkali redissolves the precipitate. Wash it on a filter with ice-cold water, and then dissolve it in weak acetic acid, which leaves a brown matter. This consists of extract formed during the washing by the contact of air. Having filtered the solution, throw down the tan by adding acetate of lead. The precipitate must be welledulcorated with water, during which its colour passes from white to yellow, and must be then decomposed by sulphuretted hydrogen. The filtered liquid is without colour, and leaves, by evaporation in a vacuum with a deliquescent salt, the tan in hard transparent scales, of a light yellow colour, which, exposed to air, and especially to light, assume a deeper yellow tint. From this dry matter, ether extracts tan only, leaving the extract.

The general properties of tan are the following:—Pure tan is colourless; when coloured, it is owing to the action of air. It is easily reduced to powder; is not deliquescent; and dissolves in water with great facility. It cannot, as is generally represented, be moulded between the finger and thumb. By distil-

lation it gives no ammonia, but yields a yellow oil, and a liquid which, on standing, deposits crystals of a nature entirely different from gallic acid, for they change the colour of solutions of iron, not to black, but to yellowish green, and cause a verdigris coloured precipitate.

The tan of oak bark is precipitated by most acids except the acetic. The precipitate is adhesive, owing to the mixture of a compound of acid and extract. By adding boiling water, the whole is dissolved, and the compound of acid and extract mostly precipitates on cooling. From the remaining liquid pure tan may be prepared in the manner already stated.

The saturated compounds of tan with acids have not a sharp taste, but are so purely astringent that the presence of an acid would not be suspected. In a pure state, they are soluble in water, but are precipitated by an excess of acid.

With salifiable bases, tan gives very remarkable compounds. The neutral tannates of potassa and ammonia are sparingly soluble in cold water, but dissolve in hot water; from which they precipitate on cooling, in a form resembling that of an inorganic earthy salt. The tan of oak bark decomposes emetic tartar, and takes the place of a part of the oxide of antimony. If we employ an infusion of galls, the gallic acid combines with the oxide of antimony, and composes a gallate of antimony, in fine scales resembling boracic acid. Alkalis, both pure and carbonated, precipitate tan, with the exception of ammonia. So also do earths, and salts with earthy bases; and several with metallic bases.

Tan is not soluble in absolute alcohol, but the dilution of that fluid, even with no more water than will bring its sp. gr. to .818, renders alcohol a solvent of tan. It is soluble in ether, especially when heated.

From the watery solution of tan almost all acids, added in excess, precipitate it. Nitric acid, however, produces a different effect; and, probably, by imparting oxygen, converts tan into a yellowish brown matter, which is soluble in alcohol. Chlorine produces a similar change; and peroxide of tin converts it into a substance resembling extract, probably by communicating oxygen.

Green sulphate of iron effects no change in the solution of tan, but the red or per-sulphate occasions a dark bluish precipitate. This precipitate differs from gallate of iron in being

decomposed by acids, the tan being thus separated. An excess of the red sulphate re-dissolves the precipitate, and affords a black or dark blue liquor, but the precipitate re-appears when the disengaged acid is carefully saturated by an alkali. By union with tan, the red sulphate is de-oxidized, the salt probably becoming the green sulphate, and the oxygen passing to the tan. Tan is capable, also, of uniting with oxide of lead in different proportions, forming a tannate and sub-tannate of lead. (Berzelius, 94 Ann. de Ch. 319.) The tannate consists of

Tan .....	65.79	.....	100
Oxide of lead.....	34.21	.....	52
<hr style="width: 20%; margin: 0 auto;"/>			
100.			

The sub-tannate contains  $1\frac{1}{2}$  time as much base as the neutral tannate.

*Tanno-gelatine*.—The watery solution of tan, poured into one of glue (inspissated animal jelly), converts it immediately into a coagulum, insoluble by boiling water, which has the elastic properties of the gluten of wheat. Hence infusion of tan is used as a test of the presence of gelatine, and, reciprocally, solution of gelatine may be used as a test of the presence of tan.

The solution of gelatine may be prepared for the purpose of precipitating tan, by dissolving isinglass in water, in the proportion of ten grains to two ounces. The precipitate, which has been called *tanno-gelatine*, consists of 54 jelly and 46 tan. An excess of the solution partly re-dissolves it. It is this property of forming with gelatine an insoluble compound, not liable to putrefaction, that fits tan for the purpose of converting skins into leather.

Dr. Duncan, jun., who has made numerous experiments on tan, observed, that the proportion of ingredients in this precipitate varies very considerably, according to the mode in which it is effected; and that insolubility in water is by no means one of its constant characters. Dr. Bostock, also, found that tan and jelly do not unite in any constant proportion, and that the compound is not, in all cases, insoluble in water. (Nicholson's Journal, xxiv. 1.) It is soluble in excess of gelatine, and more abundantly in hot than in cold solutions of jelly.

*Tanno-gelatine* is also soluble in liquid ammonia, and forms a dark brown solution, which, when spread with a brush, leaves

a film insoluble in water, oil, or alcohol. The solution, by long-keeping, changes its nature, and, when filtered and evaporated, yields a brittle shining black substance, soluble in water and alcohol, but not in ether. From the extreme facility with which it yields ammonia on being heated, it is probably a compound of that alkali with tanno-gelatine. (Faraday, in Quarterly Journ. vi. 157.)

Tanno-gelatine, boiled with solution of bi-chloride of mercury, becomes of a fawn colour, is more soft and pliable in the warm fluid, and does not, when exposed to the air, become so hard and brittle as unaltered tanno-gelatine. Its colour is also much lighter, and of an uniform brown tint. On analysis, it yields corrosive sublimate. (Ibid.)

Tan forms with fecula, or starch, a precipitate which is sparingly soluble in cold water, and very copiously in hot water. With gluten tan gives an insoluble precipitate.

Such are the general properties of tan. Even when carefully purified, it appears, however, to be a substance of by no means uniform composition, but to vary with the source from which it has been procured, and the process which has been employed to extract it. (Berzelius.) For practical uses, infusion in water is considered sufficient; but it has lately been brought from foreign parts in the concentrated form of an extract. In this country, a preference is universally given to oak bark, on account of its cheapness; but various other kinds of bark may be advantageously employed in tanning, as appears from the following Table, drawn up by Sir H. Davy, from his own experiments :

*Table of Numbers, exhibiting the Quantity of Tan afforded by 480 lbs. of different Barks, which express nearly their relative Values :*

	lb.
Average of entire bark of middle-sized Oak, cut in spring ..	29
————— of Spanish Chesnut .....	21
————— of Leicester Willow, large size ....	33
————— of Elm .....	13
————— of common Willow, large .....	11
————— of Ash .....	16
————— of Beech .....	10
————— of Horse Chesnut .....	9
————— of Sycamore .....	11

Average of entire bark of Lombardy Poplar .....	15
_____ of Birch .....	8
_____ of Hazel .....	14
_____ of Black Thorn .....	16
_____ of Coppice Oak .....	32
_____ of Oak cut in autumn .....	21
_____ of Larch cut in ditto .....	8
White internal cortical layers of Oak Bark .....	72

As a general average, four or five pounds of good oak bark are required to form a pound of leather. The operation is most perfect when performed slowly; for, if too rapidly effected, the outer surface of the skin is soon covered with a coat of leather, which defends the interior from change. In general, skins, by being completely tanned, increase in weight about one-third, the skin and the leather being each supposed dry.

*Analysis of tan.*—Berzelius analyzed tan by the combustion of perfectly dry tannate of lead with peroxide of copper. The tannate of lead had been precipitated from infusion of nut-galls. He found tan to consist of

By experiment.		By theory.	
Carbon ..	50.55 . . . . 6 atoms . . . . 36	. . . . 50.70	
Oxygen	45. . . . 4 ditto . . . . 32	. . . . 45.07	
Hydrogen	4.45 . . . . 3 ditto . . . . 3	. . . . 4.23	
	<hr/>	<hr/>	<hr/>
	100.	71	100.

On the supposition that tannate of lead is composed of an atom of each of its elements, a much higher number would be indicated for tan, *viz.* 215.4; for 52 : 103 :: 112 : 215.4. The great variety, however, in the properties of tan which have been already alluded to, are probably connected with differences of composition; and this circumstance must always occasion doubts, whether the results of analysis exhibit the true relative proportions of the elements of the species.

#### *Artificial Tan.*

Until within the last ten years, tan had been known only as a production of nature; and the processes of chemistry had effected nothing more, than its separation from the various substances with which it occurs combined. An important discovery, however, has been made by Mr. Hatchett of the artificial formation of tan from substances which unquestionably do not

contain it, but only furnish its elements. The processes for its factitious production are very numerous; but they are arranged by their author under three heads: 1st, The synthesis of tan may be effected by the action of nitric acid on animal or vegetable charcoal; 2dly, By distilling nitric acid from common resin, indigo, dragon's blood, and various other resinous substances; 3dly, By the action of sulphuric acid on common resin, elemi, assafœtida, camphor, &c. Of these various processes, I shall select the most simple, referring to Mr. Hatchett's very interesting paper for a fuller detail of the experiments. (Phil. Trans. for 1805 and 1806.)

To 100 grains of powdered charcoal, contained in a matrass, add an ounce of nitric acid (specific gravity 1.4) diluted with two ounces of water; place the vessel in a sand-heat, and continue the digestion till the charcoal appears to be dissolved. A copious discharge of nitrous gas will take place. At the end of the second day, it may be necessary to add another ounce, and sometimes even a third, of nitric acid; and to continue the digestion during five or six days. A reddish brown solution will be obtained, which must be evaporated to dryness in a glass vessel, taking care, in the latter part of the process, so to regulate the temperature, that the acid may be expelled, without decomposing the residuum. A brown glossy substance will be obtained, having a resinous fracture, and amounting, in weight, to 116 or 120 grains. This substance has the following properties:

1. It is speedily dissolved by cold water and by alcohol.
2. It has an astringent flavour.
3. Exposed to heat, it smokes but little, swells much, and affords a bulky coal.
4. Its solution in water reddens litmus paper.
5. The solution copiously precipitates metallic salts, especially muriate of tin, acetate of lead, and red sulphate of iron. These precipitates, for the most part, are brown, inclining to chocolate, excepting that of tin, which is blackish-grey.
6. Gold is precipitated from its solution in a metallic state.
7. The earthy salts are precipitated by it.
8. Gelatine is instantly precipitated from water, in the state of coagulum, insoluble both in cold and in boiling water.

Though this substance has not been subjected to ultimate analysis, yet its identity with tan can scarcely be doubted, since the two bodies agree in having the same characteristic properties. The only essential circumstance of discrimination



is, that the natural tan is destroyed, while the artificial is produced, by the agency of nitric acid; and that the artificial substance, even when formed, powerfully resists the decomposing action of this acid, which readily destroys natural tan. Even, however, among the different varieties of the natural substance, Mr. Hatchett found essential differences in the facility of destruction by nitric acid. Those of oak bark and catechu are less destructible; and, in general, the varieties of tan seem to be less permanent, in proportion to the quantity of mucilage which they contain. Infusions of factitious tan differ, also, it has been said, from those of the natural kind, in not becoming mouldy by keeping. This character, however, is not confirmed by Dr. Bostock, who has observed the artificial tan to acquire mould.

The artificial substance is a purer variety of tan than the natural one; inasmuch as it is perfectly free from gallic acid, and from extract, both of which are always present in the latter. The properties of the factitious compound vary a little, according to the mode of its preparation, principally in the colour of the precipitates, which it separates from metallic solutions. Those effected by tan, which has been formed by processes of the first class, are always brown, and by the second, pale or deep yellow.

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## SECTION XV.

### *Wax.*

It was long supposed that bees' wax is merely the dust of the stamina of plants, unchanged by any process in the economy of that animal. This opinion, however, has been shown by Huber (Nicholson's Journal, ix. 182,) to be erroneous; for bees, he has proved, continue to form wax when supplied with only raw sugar or honey. Little doubt, therefore, can exist that sugar contains all the principles of wax, and that wax is the result of a new combination of those principles, effected by the animal.

At the same time, it is equally well established that wax is also a product of vegetation. It forms the varnish, which is conspicuous on the upper leaves of many trees, and may be extracted by first removing from the bruised leaves, by means

of water and alcohol, every thing that is soluble in those fluids, then macerating the remainder with liquid ammonia, which dissolves the wax, and lets it fall, on the subsequent addition of sulphuric acid, in the form of a yellow powder. This is to be washed with water, and melted at a gentle heat. Wax exists, also, in the substance called lac, in combination with colouring matter, and is obtained in considerable quantity from the berries of the *Myrica Cerifera*, by the simple process of boiling them in water, and bruising them at the same time. The wax melts, and rises to the surface in the form of a scum, which concretes on cooling. (Cadet, Ann. de Chim. vol. xlv.)

In its ordinary state, wax of every kind has considerable colour and smell. It may be deprived of both by exposing it, in thin laminæ, to the action of the light and air, or still more speedily by chlorine gas. It melts at 145° Fahr. When bleached it has the following properties:

Its specific gravity is about .960, water being .1000. When heated, it melts at about 155° Fahr., or at from 7° to 10° higher than unbleached wax, and forms a transparent fluid, which gradually acquires consistency, till at length it returns to a solid state. If the heat be raised, it boils; and a portion of oil distils over, in which a little stearic acid has been found, but no oleic nor sebacic acids. By a still higher heat it is decomposed, and a quantity of olefiant and hydro-carburet gases is developed, the condensible products now containing a little sebacic acid. (An. of Phil. Nov. 1827.) The residuum of charcoal bears only a small proportion to the wax which has been decomposed. Wax is insoluble in water, nor is it changed by long keeping in contact with water. Boiling alcohol dissolves about one-twentieth its weight of wax, four-fifths of which separate on cooling; and the remainder is immediately precipitated by the addition of water. Or if the alcoholic solution be cooled 10° or 20° below the freezing point, a large quantity of white matter separates, which is wax; and there remain in solution the colouring principle, and an acid substance, which strongly reddens litmus. This fluid, on evaporation, leaves a fatty substance of the consistence of butter, of a yellow colour, melting at 116° Fahr. (Quart. Journ. xv. 384.) Boiling ether dissolves about one-twentieth of its weight of wax, but lets the greater part fall on cooling.

Caustic fixed alkalis convert wax into a saponaceous com-

pound, soluble in water. The *punic wax* of the ancients was a soap composed of 20 parts of wax and 1 of soda. A heated solution of ammonia dissolves wax, and forms a kind of emulsion. On cooling, the wax rises to the surface in flocculi.

Volatile oils dissolve wax when heated along with it; but a great part separates again on cooling of a softer consistence, and probably therefore containing some of the oil. Fixed oils unite with wax, and form a sort of compound well known in pharmacy under the name of *cerates*. When applied to the purpose of candles, the brittleness of wax is corrected by a little tallow.

Acids appear to have very little action on wax, unless they are concentrated and heated, when a mutual decomposition ensues.

From the results of its combustion, Lavoisier inferred that wax consists of

82.28	carbon
17.72	hydrogen
100.	

Gay Lussac and Thenard, and Dr. Ure, have analyzed yellow wax by combustion with peroxide of copper, and deduced its elements to be

Carbon .....	81.784	....	80.69
Oxygen .....	5.544	....	7.94
Hydrogen .....	12.672	....	11.37
		100. (G.L.)	100. (U.)

The atomic constitution most consistent with these results is,

Carbon .....	13 atoms	....	78	....	80.41
Oxygen .....	1 atom	....	8	....	8.26
Hydrogen ....	11 atoms	....	11	....	11.33
			97		100.

But it is not improbable, as Dr. Ure has remarked, that an atom more of hydrogen may exist in wax than has been discovered by analysis, and that it may consist of 12 atoms of olefiant gas + 1 atom of carbonic oxide.

*Myrtle wax*, it appears from the experiments of Dr. Bostock, differs from bees' wax in being more fusible (*viz.* at 109° Fahr.), and in being soluble, to a greater amount, both in ether and in alcohol. Dr. John ascertained that it is only one part of this

wax that is taken up by alcohol, while the other remains undissolved. To the first he has given the name of *cerin*. It precipitates again as the alcohol cools; is of the same sp. gr. as water; has the consistency of wax, but a much lower melting point, *viz.* 108° to 110° Fahr. The insoluble part, which he has called *myricin*, is insoluble in ether and alcohol at all temperatures. Its specific gravity is 0.900. The term *cerin* has also been applied by Chevreul to a substance resembling wax, which slowly separates from alcohol after being digested on cork. The vegetable wax from Brazil, though it appears, from the experiments of Mr. Brande, to possess the principal characters of common wax, differs from it in some properties, and also from myrtle wax. (Phil. Trans. 1811, p. 267.)

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## SECTION XVI.

### *The Bitter Principle.*

The bitter taste of certain vegetables appears to be owing to the presence of a peculiar principle, differing from every other substance in its chemical properties. It may be extracted from the wood of quassia, the root of gentian, the leaves of the hop, and several other plants, the fruit of the colocynth, &c. by infusing them for some time in cold water. The characters of this substance have been attentively examined by Dr. Thomson, who enumerates them as follows. (System of Chemistry, 6th edit. iv. 50.)

When water, thus impregnated, is evaporated to dryness by a very gentle heat, it leaves a brownish yellow substance, which retains a certain degree of transparency. For some time it continues ductile, but at last becomes brittle. Its taste is intensely bitter.

When heated, it softens, swells, and blackens; then burns away without flaming much; and leaves a small quantity of ashes.

It is very soluble in water, and in alcohol.

It does not alter blue vegetable colours.

It is not precipitated by the watery solution of lime, baryta, or strontia; nor is it changed by alkalis.

Tincture of galls, infusion of nut-galls, and gallic acid, produce no effect.

Of the metallic salts, nitrate of silver and acetate of lead are the only ones that throw it down. The effect of nitrate of silver cannot be ascribed to the presence of muriatic acid, since nitrate of lead produces no change in the solution. The precipitate by acetate of lead is very abundant; and that salt, therefore, affords the best test for discovering the bitter principle, provided no other substances, capable of decomposing it, be present.

Another modification of the bitter principle has been extracted, by M. Chenevix, from unroasted coffee. The infusion of the berries was mixed with muriate of tin, when a precipitate appeared, which was well washed, then diffused through water, and decomposed by sulphureted hydrogen gas, which carried down the tin. The remaining liquid, evaporated to dryness, gave a semi-transparent substance not unlike horn. This substance did not attract moisture from the air; was soluble in water and alcohol; and the solution, on adding alkali, became of a garnet red. Solution of iron gave it a fine green tinge, or, when very concentrated, threw down a green precipitate; and muriate of tin occasioned a yellow sediment. It was not affected by solution of animal gelatine.

From the experiments of Mr. Hatchett, it appears that the bitter principle is artificially formed, along with tan, by the action of nitric acid on indigo. When thus procured, Haussman found it to be accompanied with another product, to which Chevreul has given the name of acid of indigo. Mr. Donovan has also composed it by the action of strong nitric acid on an equal weight of sugar. In the residual matter, which is thick and tenacious, its presence is disguised by the sourness of the malic acid, but becomes sensible when this is neutralized by lime. This bitter principle, he conceives, may exist in unripe fruits, and may afford, accordingly as it is modified by vegetation, either sugar or vegetable acids. (Phil. Trans. 1815.)

When obtained from indigo, the colour of this principle is a deep yellow, and its taste intensely bitter. It is soluble in water and alcohol, and is susceptible of a regular crystallized form. It unites with alkalis, and composes crystallizable salts.

Its compound with potassa detonates when struck with a hammer, and inflames like gunpowder when thrown on hot charcoal. On the whole, it appears better entitled to rank as a distinct principle, than that which is extracted, by infusion, from vege-

tables. It must be remembered, however, that by the action of nitric acid on indigo, several products are formed. (See page 304 of this volume.)

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## SECTION XVII.

*Of Native Vegetable Alkalis.*—*Morphia, Strychnia, Brucia, Delphia, Picrotoxia, Atropia, Veratria, &c.*

The affinities, which produce in living vegetables so many acids, appear also to be capable of giving rise to a variety of alkaline substances, several of which have been discovered and identified during the few last years. So far as is yet known, the processes, by which they are obtained, effect nothing more, than their separation from the vegetables in which they existed ready formed; and they are not, as some able chemists (Robiquet for instance) have supposed, the *products* of the agents employed in their preparation. With respect to quinia, this has been fully established by MM. Henry and Plisson, in a memoir which I shall have occasion to notice in this section. These vegetables are, for the most part, distinguished by very powerful effects on the animal system, produced, it should appear, by an alkaline ingredient peculiar to each species; and a few of the active principles, thus detached, have already become important instruments in the hands of the physician. It is chiefly from their habitudes of chemical combination, that these new substances are classed among alkalis, which they resemble in the power of neutralizing acids, and of affording with them compounds analogous to the salts, which result from the union of acids with the alkaline substances that have been long known. They have all, however, weaker affinities for acids, than belong to alkalis of the latter class; their powers of neutralizing acids are extremely feeble; and their equivalent numbers consequently very high. Hence they have been termed, not improperly, by some chemists, *alkaloids*. With tincture of galls, they afford, especially those which are most active on the animal economy, an abundant white precipitate, soluble in alcohol. (Pelletier.) They are destructible, both when separate and in combination, at low degrees of heat; and ammonia is evolved, a sufficient proof of their containing nitrogen. At first they were distinguished by names ending in *ine*, as morphine, strychnine, &c.;

but, for the sake of conformity to the nomenclature of other alkalis, their names have since been modified, and the termination in *a* is now limited to those substances which have alkaline properties, that in *ine* being applied to vegetable principles which are not alkaline.

Besides these alkalis of feeble energy, it has been discovered by Dr. Peschier, of Geneva, that potassa, which had been long extracted from the ashes of plants, exists ready formed in their juices, and may be obtained by agitating pure magnesia with the liquor obtained by pressure or decoction of any part of the vegetable, except its fruit. In most plants, the potassa is united with oxalic or tartaric acid, which form insoluble compounds with magnesia; but in borage the potassa is combined with nitric acid, which magnesia has not the power of detaching from that alkali. (Ann. of Phil. xii. 336.)

#### ART. 1.—*Morphia.*

Opium, and other vegetable products possessed of narcotic power, are composed of several of the vegetable principles that have already been enumerated. Besides these, however, they contain a peculiar one, in which the narcotic virtue resides. It was first extracted from opium by Derosne in 1803 (Annales de Chimie, vol. xlv), but his process has been superseded by others, better adapted to afford the narcotic principle in a state of purity. In 1817 Sertuerner, of Eimbeck in Hanover, recommended the following method of obtaining morphia. (Ann. de Ch. et de Phys. v. 39.) Rub together in a mortar eight ounces of powdered opium, two or three ounce-measures of acetic acid, and a little cold distilled water; then add two or three pints of water, and strain the liquor. Add to it a solution of ammonia, and evaporate the liquor to one-fourth. The morphia is precipitated, and may be separated by filtration. The liquid part is a compound of ammonia with the acid ingredient of opium.

A better method of separating morphia, proposed by Robiquet, and, I believe, the one most commonly practised, is as follows: (Id. v. 379.) A concentrated solution of a pound of opium in water is to be boiled with 100 grains of pure magnesia, during a quarter of an hour. A greyish deposit is formed in considerable quantity, which is to be washed first with cold water, and next with hot and weak alcohol, which takes up a small quantity of morphia and much colouring matter. It is afterwards washed

with a little cold and concentrated alcohol, and then boiled with a sufficient quantity of the same fluid, which, at that temperature, dissolves morphia. On cooling, morphia is deposited a little coloured; but by repeating the operation three or four times, it may be obtained colourless, and crystallized in regular parallelepipeds with oblique faces.

Robinet has applied, to the extraction of morphia from opium, his method of analyzing vegetable substances by saline solutions. He digests sliced opium in six times its weight of a solution of common salt, sp. gr. 1.114, and again with four times its weight of the same fluid. The liquids are united, and submitted to evaporation. As soon as the common salt begins to crystallize, a brown substance, fluid and seemingly resinous, swims on the surface of the liquor; the evaporation is continued to dryness, and the residue digested in alcohol of sp. gr. .827. After some hours digestion, the alcohol is decanted, and replaced by three fresh quantities of the same fluid in succession. Evaporation of the alcoholic liquid, by a water-bath, produces a mass slightly coloured, formed of small needles in mamillary groups. This mass is washed with a little alcohol, dried, and redissolved in hot water, from which, on cooling, a crystallized salt is deposited. The alcoholic and watery mother liquids united, and abandoned to spontaneous evaporation, give a further product of the same salt. (Ann. de Ch. et de Ph. xxx. 208.)

This salt Robiquet considers as compounded of morphia, and an acid; to separate the acid ingredient, he adds a solution of sub-acetate of lead, and obtains a precipitate which he decomposes by sulphureted hydrogen. The liquid becomes very acid, and on evaporation affords white crystals. For this acid, Pelletier has proposed the name of *codeic acid*, from the head of the poppy. Instead of morphia, Chaussier suggested the name of *narcéine*, which Robiquet prefers, and the compound of the two (codeate of morphia) he expresses by the term of *sedative salt of Robinet*. It is proper, however, to observe that Robiquet considers the supposed codeate as a true muriate of morphia. (Ann. de Ch. et de Ph. xxxi. 73.)

Subsequently to the publication of the foregoing process, Robinet has communicated to the Acad. de Médecine, some new facts relative to the preparation of morphia. Having operated on the residue left by the action of muriatic acid on opium, and precipitated the morphia from the muriatic solution, he passed



a current of carbonic acid gas through the solution, to precipitate the excess of lime. This precipitate was found to be mixed with a very large proportion of morphia, separable, it is to be presumed, by the action of hot water. The washings of the precipitate being examined, were found free from morphia. At the same meeting, M. Henry observed, that from experiments made at La Pharmacie Centrale, it appeared that much more morphia was obtained by those processes, in which lime had been used to precipitate morphia, than by those in which magnesia had been employed. (Quart. Journ. N. S. ii. 216.)

Besides these processes, Dr. Thomson has found it easy to extract morphia by pouring liquid ammonia into a strong infusion of opium. Impure morphia is thus precipitated, which may be purified by the ordinary method, or by solution in acetic acid and digestion with animal charcoal. (Ann. of Phil. N. S.) Mr. Hottot, also, has described a method of extracting morphia, for which it is sufficient to refer the reader to the Quarterly Journal of Science, xviii. 399; and M. Tilloy, in the same journal (N. S. ii. 216), gives a method of obtaining it from dry poppy-heads. The average produce from a pound of good opium, Mr. Brande estimates at about 500 gr.; but expresses his doubts whether the whole of the morphia can be obtained from opium, by any process hitherto employed. (Man. of Pharmacy, p. 128.)

Pure morphia is perfectly white, has a pearly lustre, is destitute of smell, but has an intensely bitter taste. It dissolves in boiling water only in small proportion, but is very soluble in heated alcohol and ether, and the solutions are intensely bitter. By evaporation, they yield crystals, the primary form of which Dr. Thomson states to be a right rhombic prism. The watery and alcoholic solutions affect test papers like an alkali, and Robiquet found this property to be most distinct in morphia prepared by the intervention of magnesia, though proved, by its complete destruction by burning, to be free from any portion of that earth. It forms neutral salts with acids, and appears, therefore, to approach closely in its characters to an alkali, which it also resembles in decomposing the compounds of acids with metallic oxides. Acetate of morphia, from its ready solubility, appears to afford the best method of exhibiting this substance as a medicine.

Morphia fuses at a moderate heat, and resembles melted sul-

phur. On cooling from this state, it crystallizes. It unites with sulphur, but is incapable of forming soap with an oil.

Its effects on the human body are those of a most violent poison. Three-half-grains, taken in succession with intervals of half an hour by the same person, produced violent vomiting and alarming faintings. To discover its presence in the contents of the stomach, or intestines, when it has been intentionally administered as a poison, directions have been given by M. Lassaigne. (Ann. of Phil. N. S. viii. 223.)

Tinctures of opium, it is observed by Sertuerner, should be prepared with pure alcohol, and kept in a place which is not very cold; for a low temperature causes a precipitation of morphia. The addition of a little acetic acid prevents this inconvenience, without diminishing the efficacy of morphia on the animal system.

The following statements have been made of the composition of morphia; but from the want of agreement among them, it is probable that the substance operated upon has not in all cases been equally pure.

Carbon	.....	72.0	....	72.02	....	69.0	....	44.72
Azote	.....	5.5	....	5.53	....	4.5	....	0.00
Hydrogen	....	5.5	....	7.01	....	6.5	....	5.59
Oxygen	.....	17.0	....	14.84	....	20.	....	49.69
		<u>100.*</u>		<u>100.†</u>		<u>100.‡</u>		<u>100.§</u>

Until these differences have been reconciled, it would be premature to assign the atomic constitution of morphia. Its equivalent number, determined by its saturating power with respect to acids, appears to be a very high one, probably not less than 325.

Another ingredient of opium is the *meconic acid*, which, according to Robiquet, is best obtained from the residuum of the magnesian salt, left undissolved by alcohol in the process for extracting morphia. This residue may be dissolved in very weak sulphuric acid, and to the solution muriate of baryta may be added. A rose-coloured precipitate falls, consisting of sulphate and meconate of baryta. This is to be digested a con-

\* Brände, Quart. Journ. xvi. 284.

† Dumas and Pelletier, An. de Ch. &c. xxiv. 163.

‡ Bussy, Ann. of Phil. N. S. vi. 229. § Thomson.

siderable time with hot sulphuric acid largely diluted. When the filtered liquor is sufficiently reduced by evaporation, the meconic acid shoots, even before cooling, into coloured crystals. To obtain it pure, it must be washed with a small quantity of water, then dried, and sublimed at a gentle heat. Dr. Hare extracts it more simply by adding sub-acetate of lead to an aqueous infusion of opium, collecting and washing the meconiate of lead, and passing sulphureted hydrogen through the precipitate diffused through water. The liquid becomes of a reddish amber colour, and furnishes by evaporation crystals of the same hue. (Quart. Journ. N. S. 217.) It may, however, be doubted whether the acid thus obtained is any thing more than the codeic acid of Robinet, already alluded to.

*Meconic acid* requires for its fusion a temperature considerably above that of boiling water. It reddens vegetable blues, and is extremely soluble in alcohol and in water. Its distinguishing character is that it produces an intensely red colour in solutions of the per-salts of iron. Sertuerner did not find that when taken into the stomach, it is capable of producing any of the effects of opium.

The salt of Derosne, it appears from the experiments of Robiquet, is not, as Sertuerner supposed, a compound of morphia and meconic acid. The watery solution of opium, freed from morphia and meconic acid, contains another acid, characterized by a different train of properties, which may be separated by a process somewhat circuitous. (Ann. de Chim. et de Phys. v. 285.) This acid is not volatile, and has no peculiar action on the salts of iron. With morphia it affords salts that are readily soluble in alcohol and in water. Morphia and the salt of Derosne appear, from the experiments of Robiquet, to be both ingredients of opium, which are different, and independent of each other. On this subject, there seems to be a degree of obscurity, which can only be removed by distinctly ascertaining the characters of the acid, existing in the salts of Derosne and Robinet, and comparing them with those of meconic acid.

Beside the ingredients which have already been mentioned, opium contains an extractive matter, which forms with morphia a compound almost insoluble in water, but very soluble in acids. A considerable proportion of resin, soluble by alcohol, and precipitable by water, and a small quantity of caoutchouc, or a substance analogous to it, which is not soluble in unwashed

ether, but is soluble in spirit of turpentine, enter also into the composition of opium. These are entirely destitute of sedative properties, when received into the stomach. They remain after acting on opium first with water, and afterwards with muriatic acid. When the residue is digested with alcohol, the resinous matter is taken up; and from the remaining mass, which has resisted the action of alcohol, the caoutchouc may be extracted by rectified ether. This fluid, when digested on opium, or on what remains after the action of saline solutions and alcohol, in Robinet's process, when filtered, and evaporated at a gentle heat, yields also a crystallized substance, not at all alkaline, to which the name of *narcotin* has been given. It is contaminated with a little oil and caoutchouc, is insoluble in water, and scarcely soluble in alcohol. The exciting and stimulating effects of opium have been ascribed to this substance; and Dr. Hare attests that the alcoholic tincture, made from opium which remains undissolved after digestion with ether, is free from these pernicious qualities. Narcotin has been analyzed by Pelletier and Dumas with the following results:

Carbon .....	68.88
Azote .....	7.21
Hydrogen .....	5.91
Oxygen .....	18.00

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100.

#### ART. 2.—Of *Strychnia*.

*Strychnia* was extracted by Pelletier and Caventou, in 1818, from the fruit of the *strychnos nux vomica*, and *strychnos ignatia*. The bean was rasped down as small as possible, and then exposed to the action of heated nitric ether. The residue, thus deprived of a quantity of fatty matter, was digested in alcohol, added in successive portions as long as it continued to dissolve any thing. The alcoholic solutions were evaporated, and the residue dissolved in water. From the watery solution, liquid potassa threw down a white crystalline precipitate; which was *strychnia*. It was purified by washing it with cold water, dissolving in alcohol, and crystallizing it. *Strychnia* was separated also from the bean of the *strychnos ignatia* by the use of magnesia, in the same manner as Robiquet had obtained morphia from infusion of opium. Another process for obtaining *strychnia* has been described by M. Ferrari. (Quart. Journ. xvi.

170.) It appears, too, from the experiments of Pelletier and Caventou, to be separable, in a remarkably pure state, from the poison of the Upas tree. (Lib. cit. xviii. 176.) A substance also analogous in some respects to strychnia, but differing from it in others, has been discovered in the inspissated juice, called *curare*, used by the Indians to poison their arrows. (Ann. de Ch. et de Ph. xxxix. 24.)

Strychnia crystallizes in very small four-sided prisms, terminated by four-sided low pyramids. It is anhydrous, and has no affinity for water; it is white, intensely bitter, destitute of smell, fusible, but not volatile at moderate temperatures, very sparingly soluble in cold water, and even in hot water, of which it requires for solution 2500 times its weight. But though it is not soluble in less than from 6 to 7000 parts of cold water, the solution may be farther diluted with 100 times its volume of water without losing its taste. It is one of the most virulent and active poisons yet discovered. Half a grain, blown into the throat of a rabbit, brought on locked jaw in two minutes, and in five minutes proved fatal.

Strychnia acts as a base to acids, and forms a distinct set of salts, which are described in the Annals of Philosophy, xvi. 30, and in the Ann. de Ch. et de Phys. x. 142. Its equivalent number, derived from its power of neutralizing acids, which is very feeble, is probably not less than 380. The mean of two analyses of strychnia, by Pelletier and Dumas, afforded the following results:

Carbon . . . . .	78.22
Azote . . . . .	8.92
Hydrogen . . . . .	6.54
Oxygen . . . . .	6.38
	100.06

#### ART. 3.—Of *Brucia*.

This substance was extracted by Pelletier and Caventou from the bark of the *brucia antidysenterica*. The bark was first digested in sulphuric ether, and then in alcohol; the alcoholic solution evaporated; and the dry residuum dissolved in water. This solution was saturated with oxalic acid, and evaporated to dryness. Alcohol, digested on the residue, took up the colouring matter, and left the oxalate of *brucia* pure. This salt was decomposed either by lime or magnesia, which formed

insoluble salts with the oxalic acid, and left the brucia soluble in water, of which it requires 500 parts at 212°, and 850 at common temperatures.

Brucia crystallizes in oblique prisms with parallelograms for their bases, which contain water in combination. To strychnia it appears to be allied in the same manner as quinia is to cinchonia, and accompanies it in the nux vomica. It has a bitter taste, but less so than strychnia; its taste is more acrid, however, than that of strychnia, and continues for a longer time. From strychnia it differs, too, in having a strong affinity for water. It melts when heated to a little above 212°, and congeals on cooling into a mass resembling wax. It dissolves in sulphuric and other acids, and neutralizes them, affording a distinct class of neutral salts. (See Ann. of Phil. xv. 311, or Ann. de Chim. et de Phys. xii. 113, and xxiv. 176.) It is reddened by nitric acid, which strychnia is not. Its composition has been determined by Pelletier and Dumas to be as follows:

Carbon .....	75.04
Azote .....	7.22
Hydrogen .....	6.52
Oxygen .....	11.21
	100.

#### ART. 4.—Of *Delphia*.

This alkaline principle was detected in 1819, by MM. Lassaigne and Feneulle, in the seeds of the *delphinium staphysagria*, or *stavesacre*, in which it exists united with malic acid. The seeds were well cleaned and reduced to a pulp; then boiled with water; and the fluid part separated by a filter. The liquid was boiled, for some minutes, with a quantity of pure magnesia. The solid part of this mixture was then separated by a filter, and digested in boiling alcohol. From this solution, by evaporation at a gentle heat, delphia was obtained in a state of tolerable purity.

Delphia is a white powder, having a crystalline texture while moist, but becoming opake by exposure to air. Its taste is intensely bitter and acrid; it is destitute of smell. It melts when heated, and resembles liquid wax, and on cooling becomes hard and brittle like resin. Cold water does not dissolve a sensible portion, though it acquires an acrid taste. Alcohol and

sulphuric ether dissolve it readily, and the former solution gives a green colour to syrup of violets, and restores the blue colour of litmus, which has been reddened by vinegar.

Delphia unites with acids, and forms neutral salts, which are all very soluble in water, and have a very acrid and bitter taste. (Ann. of Phil. xvi., or Ann. de Chim. et de Phys. xii.)

#### ART. 5.—Of *Picrotoxia*.

This name has been given by Boullay to the acrid narcotic principle residing in the *cocculus indicus*, the fruit or berry of the *menispermum cocculus*. From a strong infusion of the seeds, ammonia, added in excess, precipitated a white granular crystalline powder. This powder, after being washed with cold water, partially dissolved in alcohol without colouring it; and on the spontaneous evaporation of the alcohol, was separated in beautiful silky needles. Similar crystals were obtained by adding pure magnesia to an alcoholic infusion of the seeds. A greyish deposit was formed, which, after being lixiviated with boiling alcohol, afforded crystals as before. They are white, and have the shape of four-sided prisms. Their taste is disgustingly bitter. One hundred parts of boiling water dissolve only four of picrotoxia, and of this one-half is deposited on cooling. The solution does not affect vegetable blue colours. Alcohol of the specific gravity .810 dissolves one-third its weight of picrotoxia. The addition of a little water throws down a precipitate, which a larger quantity redissolves.

Sulphuric acid has no remarkable action on picrotoxia. Nitric acid dissolves it, and forms a yellowish green solution, which, when heated and evaporated, yields oxalic acid. It dissolves in acetic acid, and is precipitated by carbonate of potassa. It is soluble also in weak solutions of the pure alkalis. The salts of picrotoxia are described in the Annals of Philosophy, xvi. 33. But its claim to be considered as an alkali has been rendered questionable by the experiments of Casaseca, which tend to prove that it is not a salifiable base, but rather a peculiar bitter principle, as Boullay himself at first described it. (Ann. de Ch. et de Ph. xxx. 315.) The more recent analysis by Casaseca has shown, also, that no peculiar acid exists that can be entitled to be considered as the menispermic. (Ann. de Ch. et de Ph. xxx. 307.)

ART. 6.—*Of Atropia.*

In the analysis of the leaves of the *Atropa Belladonna*, M. Brandes found that pure alkalis precipitated, from the decoction of the leaves in water, a substance which had alkaline properties like morphia. He boiled two pounds of the dried leaves in repeated quantities of water, mixed the decoctions, and added a little sulphuric acid, which rendered the solution thinner, and enabled it more readily to pass the filter. The decoction was then supersaturated with potassa, by which he obtained a precipitate that, after being washed with pure water and dried, weighed 89 grains. It consisted of small crystals, from which, by repeated solution in acids and precipitation by alkalis, the new alkaline substance, *atropia*, was obtained in a state of purity. It has since, however, been shown by M. Runge (*Ann de Ch. et de Ph.* xxvii. 32) that pure alkalis and lime-water decompose *atropia*, and that it is better to add hydrate of magnesia (precipitated from the sulphate by caustic potassa, and purified by copious washings) to the decoction of belladonna; to evaporate to dryness; and to extract the *atropia* from the dry mass, first reduced to powder, by boiling alcohol.

The external appearance of *atropia* varies considerably according to the mode of its preparation, being either granular, or flaky, or gelatinous, like precipitated alumina. When perfectly pure, it is snow white, otherwise it has a yellow tinge. It is quite tasteless.

Cold water has scarcely any effect upon dried *atropia*, but dissolves a minute portion when recently precipitated, and boiling water dissolves still more. It is very sparingly soluble in cold alcohol, but boiling alcohol dissolves it readily, though less abundantly than morphia, and on cooling the greater part is again deposited. Ether and oil of turpentine had little effect upon it even at a boiling heat. Hot oil of almonds dissolved a much larger quantity of it, and seemed to become less fluid.

*Atropia* forms salts with acids, the greater number of which are readily soluble in water; but they cannot be obtained without such an excess of acid as affects the colour tests. There cannot, however, be a doubt that *atropia* serves as a base, and is a true alkali; and there are strong reasons for believing that its combination with sulphuric and muriatic acids are *bi-sulphates* and *bi-muriates*. At present it would be premature to assign the equivalent of this alkali.



Atropia produces violent effects on the animal system, and M. Brandes was obliged to refrain from its investigation, by the unpleasant symptoms which it occasioned. Even the vapour of its different salts produced giddiness, and dilatation of the pupils of the eyes. (Ann. of Phil. N.S. i. 263.)

#### ART. 7.—Of *Veratria*.

In July 1819, MM. Pelletier and Caventou discovered a new vegetable alkali, united with an excess of gallic acid, in the seeds of the *veratrum sabadilla*, the root of *veratrum album*, and in that of the *colchicum autumnale*. After acting upon the seeds with ether, the residue was digested in heated alcohol. By its action a coloured tincture was obtained, which, on cooling, deposited white flakes analogous to wax. The liquid portion, evaporated to dryness, was soluble in cold water, except a small quantity of fatty matter. The watery solution, gently evaporated, deposited an orange-coloured precipitate, and when this ceased to appear, acetate of lead was poured into the residuary liquor, which had still a deep colour. Immediately a very abundant yellow precipitate fell, which was separated by a filter; and the liquid, which passed through, was almost colourless. It contained, beside other substances, acetate of lead, from which the lead was precipitated by sulphureted hydrogen. To the liquid, filtered and concentrated by evaporation, magnesia was added, and it was again filtered. The clear liquid contained acetate of magnesia and colouring matter; the magnesian precipitate was washed with several portions of alcohol; and the alcoholic solution gave, on evaporation, a powder which was excessively acrid, and had distinctly alkaline characters.

Veratria is white and pulverulent, and destitute of smell; but when inhaled into the nostrils, it produces violent and dangerous sneezing, even when the quantity is too small to be weighed. Its taste is acrid in the highest degree, but without any bitterness. In very minute quantity, it produces dreadful sickness and vomiting, and in the quantity of a few grains would doubtless prove fatal.

It is not more soluble in cold water than morphia or strychnia. Boiling water takes up 1-1000th of its weight, and acquires an acrid taste. It is extremely soluble in alcohol; and ether also dissolves it, but in less quantity.

Veratria fuses at the temperature of 122°, and has then the appearance of melted wax; on cooling, it becomes semi-trans-

parent and amber-coloured. It restores to blue the colour of reddened litmus-paper, and saturates acids, forming with them salts which are not crystallizable, and the elements of which are so weakly combined, as to be separated by the mere action of water. Nitric acid, if heated and concentrated, alters the arrangement of its elements, and decomposes it, but does not produce a red colour, as with morphia, strychnia, and brucia. In this respect, and in affording acid salts, it approaches to picrotoxia. (Ann. de Ch. et de Ph. xiv. 69.) It has been analyzed by Pelletier and Dumas, and found to consist of

Carbon .. . . . . .	66.75
Azote . . . . .	5.04
Hydrogen . . . . .	8.54
Oxygen . . . . .	19.60
Loss . . . . .	.07
	100.

ART. 8.—Of *Hyoscyama* and *Digitalia*.

In the Annals of Philosophy, xvi. 69, is a brief notice of another alkali extracted by M. Brandes from *hyoscyamus niger*, or henbane. It is not easily altered by a high temperature, even when heated to redness with charcoal. It crystallizes in long prisms, and, when saturated with sulphuric acid, or still better with nitric acid, affords characteristic salts.

The active principle of the *digitalis purpurea* has been extracted by Mr. Royer by means of ether, in the form of a brown pasty substance, which slowly restored the blue colour of reddened litmus-paper, was very bitter and very deliquescent, and seemed capable of crystallizing from its solution in alcohol. It had great activity on the animal system. (Quart. Journ. xviii. 178.)

ART. 9.—Of *Cinchonia* and *Quinia*.

The presence of an active principle in cinchona, differing essentially from gelatine, was originally suggested by Dr. Andrew Duncan, jun., of Edinburgh (Nich. Journ. 8vo. vi. 225), and named by him *cinchonin*. It was first, however, actually exhibited in a crystalline form by Dr. Gomès of Lisbon, who obtained it from the bark of *cinchona condaminea*. By the process which he followed, it was left united with some other matter, and was mistaken for a resin. MM. Pelletier and Caventou were the first who suspected that cinchonia contained a salifiable

base analogous to morphia and the other vegetable alkalis, and verified this notion by examining its properties in a state of purity. The following process for obtaining it, is given by M. Badollier, *Ann. de Ch. et de Ph.* xvii. 273.

A pound of yellow bark, bruised small, is to be boiled for a quarter of an hour, in three pints of a very dilute solution of pure potassa. The liquid, after being suffered to cool, is then to be strained through a fine cloth with pressure, and the residuum repeatedly washed and pressed. The cinchonia, thus washed, is to be slightly heated in a sufficient quantity of water, adding muriatic acid gradually, until litmus paper is slightly reddened. When the liquid is raised nearly to the boiling point, it is to be strained, and the cinchona again pressed. To the strained liquor, while hot, add an ounce of sulphate of magnesia, and after this add solution of potassa, till it ceases to occasion any precipitate. When the liquor is cold, collect the precipitate on a filter, wash and dry it, and dissolve it in hot alcohol. On evaporation of the alcohol, the cinchonia crystallizes in delicate prisms. It may be obtained, also, more simply by the following process, described by Mr. Brande. (*Man. of Pharmacy*, p. 61.) A pound of bruised bark is to be boiled in about a gallon of water, to which three drachms of sulphuric acid have been previously added. A similar decoction is to be repeated with about half the quantity of liquid, and so on till all the soluble matter is extracted. The decoctions are then to be mixed together and strained, and powdered hydrate of lime to be added, in proportion somewhat greater than is required to saturate the acid. From the precipitate (a mixture of cinchonia and sulphate of lime) repeated boilings for some minutes with alcohol, decanting the fluid while hot, separate the cinchonia, which may be obtained by distilling off the alcohol at a very gentle heat.

*Cinchonia* thus obtained is white, translucent, crystalline, and soluble in 2500 times its weight of boiling water, but a considerable part separates on cooling. It loses no weight till heated to a degree sufficient to volatilize a portion of it; and at a temperature sufficient for its decomposition, it affords ammonia. Its taste is bitter, though long in being developed owing to its insolubility; but its acid solutions have a strong taste of Peruvian bark. It is very soluble in alcohol and ether, and sparingly so in fixed and volatile oils.

Cinchonia restores the colour of litmus, which has been reddened by an acid; unites with all the acids; and, with the

greater number, forms compounds which are perfectly neutral. The sulphate is constituted of 11.27 acid and 88.73 base. It is very soluble, has an intensely bitter taste, and forms crystals, the primary form of which is a doubly-oblique rhombic prism. (Ann. of Phil. N. S. vi. 375.) The muriate is still more soluble in water than the sulphate; dissolves in alcohol; and crystallizes in delicate prisms. The nitrate is not crystallizable. The oxalate, tartrate, and gallate of cinchonia are insoluble. Hence it is that infusion of galls precipitates the decoction of cinchonia. (See Ann. de Ch. et de Ph. xv. 289, 337; xvii. 273, 316; xxiv. 176; Ann. of Phil. N. S. ii. 316; and Quart. Journ. xvi. 282.)

In the following Table, the first column of numbers expresses the composition of cinchonia, as determined by Mr. Brande, and the second contains the results of Pelletier and Dumas. In the experiments of the former, no oxygen could be found, though it was carefully sought after.

Carbon .....	79.30	.....	76.97
Azote .....	13.72	.....	9.02
Hydrogen .....	7.17	.....	6.22
Oxygen .....	0.00	.....	7.79
	100.19		100.

It would be premature to assign its atomic constitution, but its equivalent, determined from its combinations with acids, is probably about 315.

*Quinia* was discovered by Pelletier and Caventou in the yellow bark of the *cinchona cordifolia*, and from their statement of the quantity produced annually, it appears to have become, in France, an important object of chemical manufacture. (Ann. de Ch. et de Ph. March 1827.) It may be separated by processes precisely analogous to those by which cinchonia is obtained. It is not crystallizable from its alcoholic solution, but, when dried, presents a whitish porous mass, almost insoluble in water, but exceedingly bitter. Pelletier and Dumas, however, have caused it to assume a crystallized form by fusing it *in vacuo*, and allowing it to cool very slowly, but by this treatment it loses its resinous appearance, and becomes opaque. When thus fused, it gives no indication of containing water; but if it be immersed in water, it absorbs it, becomes white and friable, and retains 3 or 4 per cent. of that fluid.

In the process for obtaining quinia, MM. Henry, jun. and

Plisson have lately made a variation, which, though not applicable to the great scale, is valuable as shortening the time of operating, and is therefore adapted to the assaying of different barks. For lime, they substitute fresh formed and still moist hydrate of lead. This they add, till the acidulated decoction is very little more than neutralized, and has assumed a faint yellowish tint. The yellowish liquid contains kinate of lead, a part of which is formed by the saturation of the kinic acid existing free in the decoction; it contains also the kinates of lime and quinia (or cinchonia); and a little yellow colouring matter, with other ingredients scarcely appreciable. The deposit consists of the colouring matter united with oxide of lead; of sulphate of lead; and free quinia.

From the liquid portion, the lead may be separated by a few drops of sulphuric acid, or by a current of sulphureted hydrogen. Then filter the liquid, and add a slight excess of liquid hydrate of lime. The quinia is easily transformed into sulphate, and gives silky white crystals. The liquid, after the action of the lime, consists of the kinate of that earth almost pure. Evaporate to a syrup, and it will form a mass which must be purified by a fresh crystallization. By alcohol, sp. gr. .837, we may precipitate the kinate of lime, and again dissolving it in water or in alcohol sp. gr. .963, submit it to a fresh crystallization. By adding solution of oxalic acid in drops, the lime is precipitated, and the kinic acid remains in solution.

Beside the combination of quinia (or cinchonia) with kinic acid, those alkaloids were discovered by MM. Henry and Plisson in the decoctions, united with colouring matter, which strongly opposes their disposition to crystallize. The affinity between these principles is indeed so strong, that the sulphate of cinchonia or of quinia, added to certain wines, precipitates their colouring matter, and renders them clear. In the decoction of cinchona, part of the alkaloid is united with a red colouring matter, forming an orange compound soluble in water, in alcohol, and in acids, which visibly decolour it. There is also another combination of the alkaloids with an insoluble red colouring matter (*rouge cinchonique*) scarcely soluble in water, but abundantly in alcohol; soluble in heated weak acids; and easily demonstrated to contain no other ingredient beside the two that have been assigned. The alkaloids exist, it appears then, ready

formed in the substances that afford them, in union with an excess of kinic acid, and with different colouring matters; and the native super-kinates may, though with difficulty, be obtained in an insulated state. (Ann. de Ch. et de Ph. xxxv. 165.)

Quinia differs from cinchonia in saturating still less acid, and in giving, with the same acid, obviously different salts. The sulphate consists of 90 base + 10 acid. It crystallizes in fine needles, which have the aspect of amianthus. These are less soluble than sulphate of cinchonia, but are fully as bitter. This salt is now very extensively used in medicine; and, in the dose of a few grains, produces all the beneficial effects of Peruvian bark with much greater certainty. Two kilogrammes of the bark afford, according to M. Henry, 64 grammes, but according to Pelletier and Caventou, only 48 grammes, of pure sulphate of quinia. Eight grains are considered as equivalent to an ounce of bark.

Quinia has been analyzed by Mr. Brande, and by MM. Pelletier and Dumas, but not with a sufficient agreement of results to enable us to assign its atomic constitution. In the following Table, the numbers in the first column are those of Mr. Brande. Its equivalent, deduced from its power of saturating acids, is probably about 360.

Carbon .....	73.80	75.02
Azote .....	13.00	8.05
Hydrogen .....	7.65	6.66
Oxygen .....	5.55	10.43
	100.	100.16

According to Pelletier and Caventou, the *Cinchona Condaminea* is composed of, 1. Cinchonia united to kinic acid; 2. A greenish fatty matter; 3. A red insoluble matter; 4. A red soluble matter (a variety of tan); 5. Yellow colouring matter; 6. Kinate of lime; 7. Gum; 8. Starch; 9. Lignin.

The other varieties of cinchonia present the same ingredients in different proportions. Vauquelin long ago found that those specimens of Peruvian bark possess the greatest medicinal efficacy, whose infusions are precipitated not only by infusion of nut-galls, but by solutions of gelatine, and of emetic tartar. The inefficacy of all these agents, when applied as tests to an infusion of Peruvian bark, was observed to take place only in those specimens, which experience had shown to be destitute of medicinal virtues.

ART. 10.—*Poison of the Curare.*

This substance, used by the American Indians for poisoning their arrows, has lately been examined by Pelletier and Petroz. They find it to consist of a flocculent green matter soluble in water, destitute of taste, and differing from albumen in non-coagulability by heat; of stearine and elain soluble by ether; and of an extremely bitter substance possessing the characters of an alkaloid. In this, the poisonous qualities of the curare reside. (Ann. de Ch. et de Ph. xl. 213.)

ART. 11.—*Of Caf ea.*

This principle was found in 1821 in coffee, by M. Robiquet, who had expected, by the agency of magnesia, to discover quinia in it, as cinchonia and the coffee plant belong to the same class of vegetables, and both possess febrifuge properties. From a brief notice in the Ann. de Chimie et de Phys. xxiv. 183, we learn that it is white, crystalline, volatile, and not very soluble in water. It has been submitted to analysis by Pelletier and Dumas with this remarkable result, that it contains a larger proportion of azote than even the greater number of animal substances, being constituted of

Carbon .....	46.51
Azote .....	21.54
Hydrogen .....	4.81
Oxygen .....	27.14
	100.

M. Pelletier, who has proposed a new process, by which it may be extracted even from damaged coffee, is of opinion that caf ea cannot properly be considered as a salifiable organic base, since it has not the power of saturating acids. (Ann. of Phil. Nov. 1826.)

## SECTION XVIII.

*Of Suber and its Acid.*

This name has been used to denote common cork-wood, which appears to be possessed of peculiar properties, especially in its relation to nitric acid.

Cork-wood appears, however, from the experiments of Chevreul, to contain several substances, which may be separated from each other by the successive action of water and alcohol, applied by means of a small Papin's digester, of a peculiar construction, which he has described in the *Ann. de Chimie*, xcvi. 149. To water thus raised above its ordinary boiling point, cork gave out an aromatic principle, and a little acetic acid, which passed over into the receiver. The watery extract contained a variety of substances, *viz.*, two colouring matters, the one yellow, the other red; an acid, the nature of which was not determined; gallic acid; an astringent matter; gallate of iron, &c. Twenty parts of cork, thus treated, left 17.15 of insoluble matter, which, when digested with alcohol, yielded three distinct substances, cerin, resin, and a peculiar oil. When the alcohol was evaporated to one-sixth, and set aside, the cerin separated in small white needles, not fusible in boiling water, but becoming soft and settling to the bottom. Cerin, thus obtained, is, in a very small degree, more soluble than wax in alcohol, 1000 parts of boiling alcohol taking up 2.42 of cerin and only two parts of wax. Nitric acid gradually dissolves cerin, and changes it into oxalic acid. Its properties differ, therefore, from those of the substance to which the same name was given by Dr. John. (See page 320.)

Of the 20 parts of cork-wood thus successively treated with water and alcohol, 14 parts remained undissolved. They consisted of suber, probably, however, not perfectly pure; but, of its properties in that state, we have as yet no accurate knowledge. (See *Ann. of Phil.* ix. 52.)

Brugnatelli first converted cork by nitric acid into an acid, having some of the properties of the oxalic and benzoic, but proved, by the subsequent investigation of Bouillon la Grange and Chevreul, to be a distinct and peculiar compound. It may be prepared from cork-wood by the following process:

To a quantity of cork, grated into powder, and contained in a tubulated retort, add six times its weight of nitric acid, of the specific gravity 1.260; and distil the mixture, with a gentle heat, as long as any red vapours escape. As the distillation advances, a yellow matter, like wax, appears on the surface of the liquid. While the contents of the retort continue hot, they are to be poured into a glass vessel, placed on a sand-bath, and constantly stirred with a glass rod, by which means the liquid



gradually becomes thick. As soon as white penetrating vapours appear, let it be removed from the sand-bath, and stirred till it becomes cold. An orange-coloured mass will be obtained, of the consistence of honey, having a strong and sharp odour while hot, and a peculiar aromatic smell when cold. On this pour twice its weight of boiling water; apply heat till it liquefies; and filter. The filtered liquor, as it cools, deposits a powdery sediment, and becomes covered with a thin pellicle. The sediment is to be separated by filtration; and the liquid reduced, by evaporation, nearly to dryness. This mass is the suberic acid. It may be purified either by saturating it with alkali, and precipitating by an acid, or by boiling it with charcoal powder.

Suberic acid has the following properties :

1. It is not crystallizable.
2. It has an acid and slightly bitter taste; and, when dissolved in boiling water, it acts on the throat, and excites coughing.
3. It reddens vegetable blues, and changes the blue solution of indigo in sulphuric acid to green.
4. Cold water dissolves about  $\frac{1}{100}$ th its weight, and boiling water half its weight.
5. It attracts moisture from the air.
6. When heated in a matrass, it sublimes, and is obtained in concentric circles, composed of numerous small points.
7. With alkalis, earths, and metallic oxides, it forms a class of salts called Suberates.

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## SECTION XIX.

### *Of Bitumens.*

Though bitumens, on account of their origin, are, with more propriety, classed among mineral substances, yet, in chemical properties, they are more closely allied to the products of the vegetable kingdom. Like vegetable substances in general, they burn in the open air, with a degree of brightness that surpasses even that of resins. By distillation *per se*, they yield weak acetic acid, an empyreumatic oil, some ammonia, and a considerable quantity of olefiant and carbureted hydrogen gases, with occasionally a small proportion of carbonic acid and

sulphureted hydrogen. They are neither soluble in water nor in alcohol, and in the latter respect they differ from resins. There can be little doubt that they have been formed originally by the decomposition of vegetables.

The bitumens have been divided into liquid and solid. Formerly it was supposed that the liquid bitumens had been derived, by a sort of natural distillation, from the solid; but Mr. Hatchett has rendered it probable that the solid bitumens result rather from the consolidation of the fluid ones. (Linnæan Transactions, 1797.)

The native bituminous substances are Naphtha, Petroleum, Mineral Tar, Mineral Pitch, Asphaltum, Jet, Pit-Coal, Bituminous Wood, Turf, and Peat. To these some writers have added Amber and the Honey-Stone.

NAPHTHA is a substance well known to mineralogists as a light, thin, often colourless oil, highly odoriferous and inflammable, which is found on the surface of the water of certain springs in Italy, and on the shores of the Caspian Sea. It may be obtained also by distilling petroleum at a low degree of heat. It has a penetrating but not disagreeable odour. Its specific gravity is about .708, or, according to Brisson, .845. Saussure found its specific gravity in its natural state to be .836, after one rectification .769, and after two .758; but it could not be rendered lighter by repeating the distillations. It does not congeal at 0° Fahrenheit.

Naphtha is very volatile, highly inflammable, and burns with a penetrating smell and much smoke. It may be distilled without alteration. By long exposure to the air it becomes thick and coloured, and passes to the state of petroleum. The addition of a little sulphuric or nitric acid produces the same change more speedily. It is not miscible either with water or with alcohol, unless the alcohol be pure, and then the latter unites with one-fifth. It combines in all proportions with sulphuric ether, petroleum, and oils, both fixed and volatile. It softens caoutchouc, but does not effect a perfect solution of it. When heated, it dissolves sulphur and phosphorus, but deposits them again in crystals on cooling.

Naphtha appears to be the only fluid we are acquainted with, in which oxygen does not exist in some proportion. This circumstance renders it of great use in preserving the new metals discovered by Sir H. Davy. When recently distilled,

they have no action on it; but in naphtha that has been exposed to the air, these metals soon oxidate; and alkali is formed, which unites with the naphtha into a kind of brown soap. When carefully rectified, Saussure did not find that it was at all altered by being kept three years in vials half full.

Its boiling point is 186° Fahrenheit. The density of its vapour is 2.833, air being 1; and at 72½° Fahr. it supports a column of quicksilver 1.78 inch in height. Dr. Thomson fixes the boiling point of Persian naphtha, sp. gr. 0.753, at 320° Fahr. and the sp. gr. of its vapour at 2.263, the temperature being 55° Fahr. A mixture of this vapour with common air burns like carbureted hydrogen gas. By its detonation with oxygen gas, Saussure determined the composition of naphtha to be

Carbon .....	87.21
Hydrogen .....	12.79
	100.*

This would indicate

6 atoms of carbon .....	36	88
5 ditto of hydrogen .....	5	12
	41	100

Dr. Thomson analyzed Persian naphtha by igniting it with peroxide of copper, and obtained gaseous products indicating 32.2 carbon + 14.8 hydrogen in 100 of naphtha, leaving a deficiency of 3 per cent. which he ascribes to azote. The proportion of the atoms of carbon to those of hydrogen, best according with these experiments, would be 14 of the former to 13 of the latter. (Ann. of Phil. xv. 307.) In his recent work, he considers the vapour of naphtha from coal as constituted of 6 volumes of gaseous carbon and 6 volumes of hydrogen gas condensed into 1 volume, but this view seems to rest on theoretical grounds only.

Dr. Ure's analysis of naphtha sp. gr. 0.857 obtained by distillation from petroleum, assigns moreover an atom of oxygen, viz.,

Carbon .....	22 atoms	132	82.5
Oxygen .....	1 atom	8	5.
Hydrogen....	20 atoms	20	12.5
		160	100.

\* Thomson's Annals, x. 118.

According to this view, naphtha should consist of 20 atoms of olefiant gas + 1 of carbonic oxide + 1 of free carbon. It is probable, however, that the two last elements are to be ascribed to the impurity of the specimen submitted to analysis, which seems to have had a greater specific gravity than belongs to highly rectified naphtha. This want of agreement between different results points out the necessity of a fresh analysis of naphtha.

PETROLEUM is considerably thicker than naphtha, and has a greasy feel. It is imperfectly transparent, and of a reddish brown colour. Its specific gravity is .878.

When distilled *per se*, a portion of colourless naphtha is first obtained; then an empyreumatic acid liquor; next a thick brown oil; and a portion of black shining coal remains in the retort.

Petroleum is highly inflammable. Sulphuric and nitric acids convert it into a thick bitumen; and exposure to the air produces the same effect more slowly. It has the property of combining with fat and essential oils, with resins, camphor, and sulphur; and, when rectified, it dissolves caoutchouc.

MINERAL TAR is thicker and more viscid than petroleum, and of a reddish or blackish brown colour. In chemical properties it resembles petroleum.

The solid bitumens are Maltha, Asphaltum, and Elastic Bitumen or Mineral Caoutchouc, besides the several varieties of Coal and Peat.

MALTHA, or MINERAL PITCH, has a brownish black colour, and little or no lustre. It is so soft that it is impressed by the nails, but does not stain the fingers. Its specific gravity is from 1.45 to 2.06. It is extremely inflammable, and burns with a bright flame, leaving only a small quantity of ashes.

ASPHALTUM is brownish black in its colour, is brittle, shining, and does not stain the fingers. Its specific gravity varies from 1.07 to 1.65. It is extremely inflammable, and burns with a yellow flame. By distillation *per se*, it yields a light brown oil resembling naphtha, a portion of water impregnated with ammonia, and a quantity of carbureted hydrogen gas. It has been analyzed by Klaproth, whose account of it may be seen in the second volume of his "Contributions."

The appropriate solvent of asphaltum is naphtha, of which it requires five times its weight. The solution is of a deep black colour, and forms an excellent varnish.

ELASTIC BITUMEN, or MINERAL CAOUTCHOUC, is a rare production of nature, and was long found only in Derbyshire; but recently it has been discovered at Montrelais, in France. It is inflammable, and burns with much smoke. By a gentle heat it is melted and converted into petroleum, maltha, or asphaltum. It resists the action of solvents. Both the English and French varieties have been analyzed by M. Henry, fils, with the following results. (Ann. of Phil. N.S. xi. 70.)

	English.	French.
Carbon .....	52.250	58.260
Hydrogen .....	7.496	4.890
Nitrogen .....	0.154	0.104
Oxygen .....	40.100	36.746
	<hr/>	<hr/>
	100.000	100.000

RETINASPALTUM is found in small quantity, chiefly at Bovey-Tracey, in Devonshire. It has no elasticity; but is brittle, and breaks with a glassy fracture. Its colour is pale ochre-yellow; its specific gravity 1.135. It melts on the application of heat, and burns with a bright flame. It is partially soluble in alcohol, potassa, and nitric acid. One hundred parts contain 55 resin, 42 asphaltum, and 3 earthy matter.

PIT-COAL is a general term, applied to several distinct varieties of minerals. These varieties have been divided by Werner into the three families of brown coal, black coal, and glance coal or mineral carbon.

I. *Brown coal* is only imperfectly bitumenized, and exhibits, distinctly, the remains of the vegetables, from whose decay it has originated. It is brown, opaque, somewhat flexible and elastic, and nearly light enough to float on water. It burns with a clear flame, and with a bituminous odour mixed with that of sulphur. In the mode of its combustion, as well as in its external appearance, it bears a considerable resemblance to wood that has been half charred.

II. *Black coal* is the substance which is commonly applied to the purposes of fuel. It shows no remains of the vegetables from which it has originated; but appears to be a compound of bitumen and charcoal; and, according to the proportion of these two ingredients, its properties vary considerably. The best kinds melt on the application of a moderate heat, and burn almost entirely away, with a clear bright flame. By distillation,

they yield a quantity of water holding carbonate and sulphuret of ammonia in solution; a large proportion of tar is obtained, which, by evaporation and fusion, forms a kind of asphaltum; and an immense production takes place of olefiant and carburated hydrogen gases, which may be advantageously applied to burning in lamps. (See vol. i. p. 452.)

In the retort, a hard heavy charcoal remains called *coke*. It contains generally a good deal of sulphur; and emits, during combustion, a suffocating smell of sulphurous acid.

The Wernerian arrangement of black coal into six subspecies, does not appear to Dr. Thomson applicable to the different kinds of coal which are found in Great Britain. He proposes four subdivisions only, which he distinguishes by the following names:

1. *Caking coal*, so called because its fragments melt at a certain temperature, and unite into one mass. The coal of Newcastle, which is carried to London, and also much of the coal found in the neighbourhood of Manchester, and in various other parts of the kingdom, belong to this species.

2. *Splint coal*, or *splent coal*, which has received its name from the splintery appearance of its cross fracture. It has also been called *hard coal* from the difficulty of breaking it. It is the sort best adapted for making coke, and extracting iron from its ores; though, when it cannot be obtained, other varieties of coal are applied to those purposes.

3. *Cherry coal*.—This coal abounds in the neighbourhood of Glasgow and in Staffordshire. It has considerable lustre, both in its principal fracture, which is slaty, and in its cross fracture, which is flat and conchoidal. It is of about the same degree of hardness as caking coal, and, being very easily frangible, there is considerable loss in mining it. It readily catches fire, burns with a clear yellow flame, and is consumed much faster than either of the foregoing species. It abounds in the neighbourhood of Glasgow and of Birmingham.

4. *Cannel coal* is a very well-characterized species. It is found of the best quality, and in the greatest abundance, at Wigan in Lancashire. Its great combustibility, and the vivid light which it emits, have occasioned its being sometimes substituted for candles. As it does not at all soil the fingers, and is easily turned by a lathe, it is made into snuff-boxes, ink-stands, and various trinkets.

The fluid and gaseous substances, obtained by the analysis of pit-coal, are to be regarded, not as mere products which pre-existed in the coal in the same state as that in which they are evolved, but as generated by the action of heat which effects a new arrangement of their ultimate elements. Dr. Thomson, therefore, considers the ultimate analysis of coal as alone capable of giving any satisfactory information of its nature. With this view he analyzed the different species, by combustion with peroxide of copper. The proportion of incombustible matter in each species was found to be as follows :

- In 100 grains of caking coal . . . . . 1.5
- In 100 grains of splint coal . . . . . 9.5
- In 100 grains of cherry coal . . . . . 10.
- In 100 grains of cannel coal . . . . . 11.

The quantity of coke formed, and of volatile matter dissipated, from 1000 parts, are expressed in the following Table :

From 1000 parts of	Weight of Coke.	Volatile Matter.
Caking coal . . . . .	774.0	226.
Splint coal . . . . .	647.3	352.7
Cherry coal . . . . .	522.5	477.5
Cannel coal . . . . .	400.	600.

The two following Tables exhibit the results of Dr. Thomson's analysis of the four different species of coal :

I. *Constituents by Weight.*

	Carbon.	Hydrogen.	Azote.	Oxygen.	Total.
Caking coal . . . . .	75.28	4.18	15.96	4.58	100
Splint coal . . . . .	75.00	6.25	6.25	12.50	100
Cherry coal . . . . .	74.45	12.40	10.22	2.93	100
Cannel coal . . . . .	64.72	21.56	13.72	0.00	100

II. *Constituents in Atoms.*

	Carbon.	Hydrogen.	Azote.	Oxygen.	Number of atoms
Caking coal . . . . .		11	3	1.5	48.5
Splint coal . . . . .	28	14	1	3.5	46.5
Cherry coal . . . . .	34	34	2	.1	71.
Cannel coal . . . . .	11	22	1	.0	34.

Dr. Ure has given different results for splint and cannel coal. (Phil. Trans. 1822, p. 471.) But as azote is not included in them, and as all the specimens of these two varieties of coal, which I have ever tried, have yielded ammonia by distillation, I cannot consider the atomic constitution, which he has assigned to these two bodies, as correct. It appears to me, however, that he is nearer the true proportion of oxygen, *viz.*, 21.05 in 100 parts of cannel coal, and 24.8 in 100 of splint coal; for the quantity of products into which oxygen enters (water, carbonic acid, and carbonic oxide), obtained by the destructive distillation of coal, indicates a considerable proportion of that element.

III. *Glance coal* appears to be chiefly pure charcoal with very little bitumen, accompanied only by a proportion of earthy matter. It is found at Kilkenny, and is common in some parts of this kingdom, where it is known by the name of *stone coal*. It burns with little or no flame; and, when submitted to distillation, yields no tar, and a sort of carbureted hydrogen gas issues in small quantity, which, from its inferior density, cannot be advantageously burned in lamps.

NAPHTHALINE.—This substance, though not a native bitumen, may be described in this place, as one of the products of the decomposition of coal. It is produced abundantly in the first and second distillations of coal tar; and separates spontaneously, especially in cold weather, from the volatile oil which comes over. Mr. Chamberlain finds (Ann. of Phil. N. S. vi. 135) that if the products of distilling coal tar be received in six different portions, the last contains so much naphthaline as to become in a few hours actually solid. About five pounds are usually thus obtained from 100 gallons of coal tar; but if the distillation be hurried towards the middle or latter end of the operation, the quantity of naphthaline is much increased. After being purified as completely as possible, from the oily matter which adheres to it, by being pressed between folds of blotting-paper it may be dissolved in heated alcohol, from which it separates again on cooling. After repeated solutions and crystallizations, it is obtained in brilliant white scaly crystals, similar to benzoic acid, but of a more silvery lustre. It is soluble in spirit of turpentine, and the solution affords crystals by evaporation. The best way of obtaining these crystals, according to Mr. Chamberlain's experiments, is to add about an ounce of naphthaline to a pint of turpentine already saturated at the tempera-



ture of the atmosphere, and to apply heat. From this liquid, when set by in a cool place, long prismatic crystals separate.

Naphthaline has a pungent and aromatic taste, and a penetrating smell, which adheres permanently to any substance that is brought into contact with it. It is smooth and unctuous to the touch. Its specific gravity is 0.7812. (Thomson.) It is less volatile than camphor, melts at about  $180^{\circ}$  ( $168^{\circ}$  Ure) and boils at  $410^{\circ}$  Fahr. On cooling, it assumes a distinctly crystalline structure.

It is not very easily inflamed; but, when set on fire, it burns with a copious dense smoke. It does not affect the colours of litmus or turmeric. It is insoluble in cold water, and very sparingly in hot water. It is readily soluble in alcohol and ether, and in both those fluids, when heated, it dissolves to almost any amount. It is soluble in fixed and essential oils; in acetic and oxalic acids, to each of which it imparts a pink colour; and in diluted mineral acids. Of all its characters, its ready disposition to crystallize is perhaps the most remarkable. These crystals are rhombic plates, the greater angle of which varies from  $100^{\circ}$  to  $105^{\circ}$ , and which are arranged so as to intersect each other and to form cells.\*

Naphthaline has been analyzed by Dr. Ure, who assigns to it the following atomic constitution. It appears to consist of

Carbon	.....	2 atoms	....	12	....	92.9
Hydrogen	.....	1 atom	....	1	....	7.1
				13		100.

The absence of oxygen, first pointed out by Mr. Brande, is confirmed by this analysis. (Phil. Trans. 1822, p. 473.) Dr. Thomson's results led him to view naphthaline as a sesqui-carburet of hydrogen, or compound of 3 atoms of charcoal and 2 atoms of hydrogen. (First Princ. i. 156.)

*Sulpho-naphthalic acid.*—When concentrated sulphuric acid and naphthaline are brought into contact, at common or slightly-elevated temperatures, Mr. Faraday finds that a peculiar acid compound is produced, probably by the union of the sulphuric acid with the elements of the naphthaline. As the new acid forms a soluble salt with baryta, it is easy to separate

\* Brande, Quarterly Journ. viii. 287; Ann. of Phil. xv. 75; Professor Kidd's Memoir in Phil. Trans. 1821, p. 214.

it, by adding carbonate of baryta, which, with sulphuric acid, composes an almost insoluble salt. From the filtered liquid, the cautious addition of sulphuric acid throws the baryta, leaving the new acid uncombined, and in a state of solution. It powerfully reddens litmus, and has a bitter acid taste. When much concentrated by evaporation, it assumes a brown colour, and, on cooling, becomes thick and ultimately solid, but deliquescent. It was found easy to obtain it dry, by exposure in a vacuum along with sulphuric acid. The solid, thus obtained, may be dissolved in water and in alcohol: with bases it forms neutral salts, called *sulpho-naphthalates*, all of which are soluble in water, most of them in alcohol, and all are combustible. The salt with base of baryta is bitter, soluble, and burns with so bright a flame, that its discoverer has named it *flaming salt*.

By the same operation that affords the above acid, another, of a different kind, is produced in small quantities; least plentifully at low temperatures, and when the naphthaline is in large proportion. It is less soluble in water; its crystals are prismatic, colourless, and transparent; and on platinum foil burn with very little flame, and rather in the manner of tinder.

As to the constitution of the sulpho-naphthalic acid, Mr. Faraday considers it as probable, though not absolutely proved, that sulphuric acid does not, during its production, undergo decomposition. If this be correct, the sulphuric acid, which the new acid contains, must have its saturating power diminished one half by union with hydro-carbon. This very interesting fact in chemical affinity has been observed by Mr. Hennell in the course of his experiments, which will be noticed in the section on ether, and also by Thenard, in the curious compound of oil of turpentine with muriatic acid, discovered by Kind. (See p. 266.)

IN PEAT or TURF, the remains of vegetable organization are generally very evident; and it consists, indeed, in a great measure, of fibres of several mosses, with occasionally whole branches, and even trunks, of various trees. It is extremely inflammable in the open air; and, when distilled in close vessels, yields products similar to those of coal. The gas, however, which is evolved, approaches more in its characters to carbonic oxide than to carbureted hydrogen. In an excellent account of this substance, given by Mr. Jameson in his Mine-

ralogy of the Shetland Isles, peat is said to contain the suberic acid. The sulphates of iron, soda, and magnesia, are, also, occasionally found as ingredients of peat; and, when in considerable proportion, impair its combustibility.

MELLILITE, or HONEY-STONE, so called from the resemblance of its colour to that of honey, is a very rare production, and has been found accompanying brown coal, in a very few parts of the continent. It is consumed when ignited in the open air, but without flame or smoke. When long boiled in water, it yields a solution, which, on being concentrated and mixed with alcohol, becomes pitchy. By continued trituration, however, it is dissolved, with the exception of some earthy flocculi. The clear liquid, decanted and evaporated, yields a brownish saline mass; from which, by two successive evaporations and solutions, needle-shaped crystals are obtained. These are the pure *mellitic acid*.

The taste of this acid is sweetish, and at the same time sour, with some bitterness. It is combustible when ignited in the air; and is decomposed by nitric acid, without the production of any oxalic acid. Dropped into the watery solutions of lime, baryta, or strontia, it gives a precipitate, which is soluble in muriatic acid. With acetates of baryta and lead, and nitrates of mercury and iron, it gives precipitates, which are soluble in nitric acid. It neutralizes the three alkalis, and affords with them crystallizable salts.

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## SECTION XX.

*Of Asparagin, Ulmin, Dahline, Inuline, Legumine, Bassorine, Fungine, Polychroite, Hematine, Nicotine, Pollenine, Emetin, &c. &c.*

By an attentive examination of the products of vegetation, some new substances have been discovered, the properties of which do not agree with those of any that have been the subjects of the preceding sections. Of this number, some cannot be considered as sufficiently investigated to be received as distinct principles; and others are limited to so few plants, that there appears to be a propriety in describing them apart from the more general products of vegetation.

*Asparagin*.—From the juice of asparagus, concentrated by evaporation, Messrs. Vauquelin and Robiquet observed a con-

siderable number of crystals to separate spontaneously. Their forms have since been ascertained by Plisson to be rectangular octahedrons, more or less modified, right rhombic prisms, and prisms with six sides. Of these, some became, after repeated crystallizations, perfectly white and transparent. They were cool and slightly nauseous to the taste; were soluble in water; and neither affected the reagents for acids nor alkalis. The infusion of galls, acetate of lead, oxalate of ammonia, muriate of baryta, and hydro-sulphuret of potassa, produced no change in the solution; and no ammonia was disengaged by potassa. When burned in a platinum crucible, they swelled up and emitted penetrating vapours, which affected the eyes and nose like the smoke of wood; and left a large proportion of charcoal, in which no traces of alkali could be discovered. Towards the close of the decomposition, an odour arose similar to that of animal matter, and inclining, also, to that of ammonia. It appears, therefore, that this substance, though crystallizable, cannot be considered as a neutral salt, for it contains neither alkali nor earth. Like other vegetable matters it appears to consist of hydrogen, oxygen, and charcoal, in proportions not yet determined, with perhaps some nitrogen.

From the juice of fresh liquorice root, Robiquet obtained a crystalline substance, to which he gave the provisional name of *agedoïte*; but it has since been shown by Plisson to be identical with asparagin. (Ann. de Ch. et de Ph. Jan. 1828.) A new vegetable principle was supposed, also, to have been extracted from marsh-mallow (*althea officinalis*) by M. Bacon, of Caen, who obtained by his method crystals of a superb emerald green colour. This colour has been shown by Plisson to be quite adventitious, and he has proved that the supposed new principle is nothing more than asparagin united with malic acid. (Id. Feb. and Oct. 1827.) In asparagin itself, however, he has discovered a peculiar acid, the *aspartic*, by decomposing with sulphureted hydrogen the insoluble salt of lead, which is formed by acting on asparagin with hydrated oxide of that metal. Long prismatic and colourless crystals are deposited by the solution, which are slightly acid to the taste, and redden litmus. They require 128 parts of cold water for solution, and are much more soluble in hot water. Alcohol does not dissolve them.

Aspartic acid, when heated, is decomposed, and produces ammonia, prussic acid, &c. It is not decomposed by being

boiled with twelve times its weight of nitric acid. By ebullition with starch for a sufficient time, the starch is changed into sugar, as it is also by quinic acid. It unites with bases, and constitutes an extensive series of salts, which M. Plisson has described under the name of *aspartates*. (Ann. de Ch. et de Ph. xl. 309.)

*Ulmin*.—In the year 1802, Klaproth received from Palermo, a substance which exudes spontaneously from a species of elm, and which, in external characters, bore a considerable resemblance to gum. It dissolved in a small quantity of water, and gave a transparent solution of a blackish brown colour, which was not, however, mucilaginous, and could not be applied to the purpose of a paste. Nitric acid precipitated from the solution a light brown substance, which was soluble in alcohol, though the gum itself resisted that solvent. Oxymuriatic acid produced a similar effect. The property of producing a resin by the addition of a little oxygen, is peculiar to this substance, and sufficiently characteristic. Dr. Thomson has proposed for it the name of *Ulmin*, and he and Mr. Smithson have paid much attention to the investigation of its properties. (See Annals of Philos. vols. i. and ii., and Mr. Smithson's paper, Phil. Trans. 1813.) It appears to be a very common vegetable product, exuding from various trees, and existing, according to Berzelius, in the bark of most. When pure, it is tasteless; sparingly soluble in water and in alcohol; not precipitated by acids, gelatine, or tan; and very soluble in alkaline carbonates, from which it is separated by acids and metallic salts. Döbereiner has converted gallic acid into ulmin; and represents the latter to be constituted of 1 atom of carbon, 1 atom of hydrogen, and 2 atoms of oxygen, but he ascribes to the atom of carbon twice the weight usually assigned to it. (Ann. de Ch. &c. xxiv. 335.)

*Dalhine*.—This substance was extracted by Layen from the bulbs of the *Dahlia* by the following process: The pulp was diluted with about its weight of water, filtered through cloth, and mixed with 1-20th its weight of pulverized chalk; then boiled for half an hour and filtered. The residuum of the bulbs was diluted with boiled water and again pressed, and the solutions, being united, were evaporated to 3-4ths of their volume, mixed with 4 per cent. of animal charcoal, and clarified with yolk of egg. From the liquor, filtered and evaporated to

a pellicle, the dahlone separated on cooling, in the proportion of about four per cent. of the bulbs.

Dahlone when pure is white, pulverulent, without taste or smell, of sp. gr. 1.356; more soluble in hot than in cold water, and insoluble in alcohol, which precipitates it from its watery solutions. It is soluble in cold potassa, but not in liquid ammonia. Sulphuric acid changes it into an uncrystallizable sugar, of greater sweetness than that formed with starch. It appears to have most analogy with starch and inulin, but differs from them in assuming a granular form, when a watery solution of it is evaporated to a pellicle; in specific gravity, &c. (Ann. de Chim. et de Phys. xxiv. 209.)

*Inulin*.—When the roots of the *inula helenium*, or elecampane, are boiled some time in water, the decoction, after standing some hours, deposits a white powder like starch, but differing in its chemical qualities. Rose, who was the first person that investigated its properties, found that it is soluble in cold water; but that it readily dissolves in four times its weight of boiling water into a liquid which is somewhat mucilaginous, and not quite transparent. After some hours, the substance precipitates from the water, in the form of a white powder; and it may also be thrown down by alcohol. When placed on burning coals, it melts as readily as sugar; emits a similar smell; and is consumed, leaving a very small residuum of charcoal. When treated with nitric acid, it yields oxalic and malic acids; or acetic acid, if too much nitric acid be employed. It differs, however, from gum in not affording, by this treatment, any saccholactic acid; and from starch (besides separating spontaneously from hot water) in yielding none of the waxy matter, which is formed when starch is digested with the same acid.

Inulin has since been examined by M. Gaultier de Claubry, who has pointed out the following characters as discriminating it from fecula or starch. It is much more soluble than starch in hot water, with which it does not form a jelly, but is deposited on cooling in the form of a white powder. It dissolves, also, in four or five times its weight of water at 140° Fahrenheit, and the solution, when evaporated, becomes viscous, but not gelatinous. With iodine, it forms a greenish-yellow compound, which is spontaneously decomposed, in part at least, in a short space of time. The inulin remains slightly coloured yellow, and retains a portion of iodine. Muriatic acid, as well as solutions

of pure alkalis, render starch gelatinous, but dissolve inulin without giving any jelly. Concentrated sulphuric acid, which carbonizes starch, and is at the same time converted into sulphurous acid, dissolves inulin without any extrication of sulphurous acid; and the inulin may be precipitated by ammonia. These properties appear to be sufficiently characteristic, to entitle inulin to be considered as a distinct vegetable substance. To obtain it in a state of purity, M. de Claubry recommends to boil the roots of elecampane in a sufficiently large quantity of water; to filter the liquor, and to evaporate it to the consistence of an extract, which is to be washed with cold water. From the washings, there falls a considerable quantity of inulin, which is to be gently dried, not however on filtering paper, as it adheres to this too firmly to be got off. (94 Ann. de Chim. 200.)

Inulin has been found by Pelletier and Caventou, in the root of the *Colchicum Autumnale*, remaining after the successive action of ether, alcohol, and water. To distinguish it from starch, they pour into a decoction of the substance, supposed to contain inulin, an infusion of nutgalls. An immediate precipitation ensues. On heating the liquor gradually, the precipitate is redissolved at about 122° Fahr. if the starch be pure, but if inulin be present, it is not redissolved till the liquid approaches 212°. (Ann. de Chim. et de Phys. xiv. 82.) Inulin constitutes an ingredient also of the roots of the *Anthemis Pyrethrum*, and of the *Angelica Archangelica*, and, according to Dr. John, of the gall nut. (Do. viii. 102.)

*Legumine*.—When ripe and dried peas are steeped, for some hours, in warm water; then reduced to a pulp in a marble mortar; and the mass, after being worked up with more water, is placed on a hair sieve, a milky liquor passes through, which, on standing, deposits all the starch it held in suspension. The supernatant liquor holds in solution, probably in a vegetable acid, a substance, first observed by Einhof, to which Braconnot has given the name of *legumine*. It imparts to the above mentioned liquid the property of frothing, when agitated with air, like a mixture of white of egg and water; but it is quite free from albumen. By gentle evaporation, the legumine separates in transparent scales, which, when removed, are soon replaced by others. When washed with hot alcohol, it becomes white, and as finely divided as starch; and being dried, is semitransparent. A green matter only, analogous to *chlorophylle*, is dissolved by the alcohol.

Vegetable acids, largely diluted, dissolve finely divided legumine with great facility. All the mineral acids, on the contrary, precipitate it by forming insoluble compounds which have an excess of acid. On boiling this precipitate with more of the same acid, it is dissolved, and on cooling resembles *starch paste*.

Legumine, heated with a little of any vegetable acid, the tartaric for instance, gives a thick mucilage, which has no acid taste. All alkalis and their carbonates, even when much diluted, dissolve it readily, whether pure or united with mineral acids. The solution is a slippery liquid, which may be blown up into bubbles like soap. The solution of legumine in weak acids, being boiled with sulphate of lime, yields a white dense coagulum. This seems to explain why leguminous vegetables are hardened, by being boiled with water containing gypsum. (Ann. de Ch. et de Ph. xxxiv. 68.)

*Bassorine*.—The gum from Bassora, supposed to be the product of a species of *cactus*, having been examined by Vauquelin and by Pelletier, has been pronounced by them to be a distinct vegetable principle. It is found also in assafoetida, bdellium, euphorbium, sagapenum, &c. It is solid, semi-transparent, insipid, and inodorous. Water, whatever may be its temperature, swells it only, without dissolving it. Dilute nitric acid dissolves it almost completely with the assistance of heat; and from this solution, alcohol precipitates a substance analogous to gum arabic. It dissolves also in acetic and muriatic acids.

*Fungin*.—This substance has been extracted by Braconnot (79 Ann. de Chim. 267) from the fleshy part of mushrooms. It may be obtained by washing off the soluble ingredients with hot water, to which a little alkali has been added. There remains a white, insipid, soft, and but little elastic substance. It has a fleshy structure, and is in a high degree nutritious, and free from deleterious properties. When dry, it burns vividly, and emits an odour resembling that of bread. By destructive distillation, it yields ammonia, and not, like wood, an acid. It differs, also, from lignin, in being insoluble in alkaline solutions, except when they are heated and very strong. Pure ammonia dissolves a portion of it, but deposits it on exposure to air.

Weak sulphuric acid has no action on fungin. The concentrated acid chars it, and sulphurous and acetic acids are formed. Muriatic acid dissolves it slowly, and converts it into a gelatinous matter. When heated with diluted nitric acid, azotic gas is



disengaged. In this property, and in the results of its putrefaction, as well as in yielding ammonia on distillation, it approaches very nearly to animal substances.

*Polychroite*.—This name has been given, by Bouillon La Grange and Vogel, to the extract of saffron prepared with alcohol. It has a very intense yellow colour, a bitter taste, and an agreeable smell. It is soluble in water and in alcohol; and the solution, by exposure to light, gradually loses its colour, which is destroyed, also, by chlorine. A few drops of sulphuric acid change the colour to a beautiful blue; and nitric acid, added in like manner, to green. Polychroite unites with lime, potassa, and baryta, and affords with those bases soluble compounds. Sulphate of iron precipitates it of a dark brown colour. By destructive distillation, it yields an acid liquor containing ammonia, and carbonic acid and carbureted hydrogen gases.

M. Henry of Paris, having recently examined polychroite, finds it to be a compound of colouring matter with a volatile oil, the former in the proportion of 42, the latter of 10, per cent. It is to the volatile oil that he imputes any activity, which saffron may possess as a medicine.

*Hæmatin* is the colouring matter of the *Hæmatoxylon Campechianum*, or Logwood, and was first recognised by Chevreul as a distinct vegetable substance. To obtain it, digest finely ground logwood, for several hours, in water of a temperature between 120° and 130°. Let the filtered liquor be evaporated to dryness, and the residue be digested for a whole day in alcohol of sp. gr. 0.835. Filter the solution, concentrate it by evaporation, then add a little water, evaporate a little farther, and leave it to itself. Small brilliant crystals will be deposited in abundance, of a reddish white colour, and a slightly bitter, astringent, and acrid taste. They are soluble in boiling water, and impart to it an orange red colour, which becomes yellow when the liquid cools, but is restored by heat. The solution on evaporation again yields crystals of hæmatin. Acids, with the exception of the sulphurous acid, which destroys its colour, render the solution first yellow and then red. Gelatin precipitates it from water in yellow flocks. (Ann. de Chim. lxxxi. 128.) When guarded from the atmosphere, a blue solution is produced by mixing potassa with solution of hæmatin; but if it be kept in contact with oxygen, the blue colour instantly changes, and gives place to a reddish yellow. All the hæmatin is thus destroyed, and from the

remaining liquid muriatic acid disengages carbonic acid. The alkaline combination of hæmatin attracts oxygen with such force, that 1.5 grain dissolved in about .08 of a cubic inch of liquid potassa, deprived about one cub. in. of atmospheric air of the whole of its oxygen, in 12 minutes. (Quart. Journ. xx. 389.)

*Nicotin.*—This is the principle in which reside the active properties of tobacco (*nicotiana*), from the juice of which it may be extracted by the following process of Vauquelin. (Ann. de Chim. lxxi. 139.) Evaporate the expressed juice to one fourth of its bulk, and pour off the fluid from the gritty matter which separates on cooling. Repeat this operation as often as any similar deposit takes place; and, when the fluid is so much inspissated that nothing farther can fall, digest it in alcohol. Distil off the alcohol, and concentrate the residual matter to dryness by a very gentle heat. Dissolve this again in alcohol, and again reduce it to a dry state. In this state, it still contains both acetic and malic acids; it must therefore be dissolved in water, and very cautiously saturated with potassa. When this liquid is distilled to dryness, a solution of nicotin passes into the receiver. By dissolving the residual matter in water, and again distilling, repeating this process several times, the whole of the nicotin may be obtained in aqueous solution. This solution is colourless; has the peculiar smell of tobacco; and occasions violent sneezing. Its taste is acrid, and it possesses poisonous qualities. According to Vauquelin it is precipitated by tincture of galls, and it approaches most nearly in its properties to the volatile oils.

*Pollenin.*—The pollen of tulips was ascertained by Professor John to contain a peculiar substance, which was at first confounded with albumen; but to which he has since given the name of pollenin. (Thomson's Annals, vii. 49.) It is insoluble in alcohol, ether, water, oil of turpentine, naphtha, carbonated and pure alkalis; and when distilled yields ammonia and an acid liquor. It has a yellow colour, and is destitute of taste and smell. By exposure to the air it putrefies, and acquires the smell of cheese. It is extremely combustible, and burns with great rapidity and flame, in consequence of which the pollen of the *lycopodium clavatum* has been often used in theatrical exhibitions to imitate lightning.

*Emetin.*—There are three different genera of plants that are employed under the name of Ipecacuanha; but it is the root of

a species of *callicocca* that is directed by the Pharmacopœia of the London College. The cortical part of the root has been submitted to a skilful analysis by MM. Magendie and Pelletier, who have obtained from it about 14 per cent. of a peculiar matter, in which the emetic virtue of the root exclusively resides, and which they have therefore called *emetin*. (Thomson's Ann. xi. 422.)

To obtain emetin, powdered ipecacuanha is to be digested with sulphuric ether, which removes a portion of fatty matter. Alcohol is then to be digested on the remainder; the tincture to be evaporated by a water bath; and the dried matter dissolved in cold water, which separates the wax. It is next to be macerated on powdered carbonate of baryta, to remove the gallic acid; again dissolved in alcohol; and evaporated once more. The emetic principle remains in the form of transparent scales, of a reddish brown colour. It has scarcely any odour; has a slightly acrid and bitter, but not a nauseous taste; deliquesces in the atmosphere; is soluble in water and in alcohol in all proportions; and is incapable of being crystallized. The watery solution, Vauquelin remarks, being heated, scarcely becomes warm, ere a pellicle forms on the surface and soon breaks and swims in the liquid. This, when dried, is destitute of smell, but has an intensely acrid taste.

Emetin is decomposed by a heat exceeding that of boiling water, but gives no ammonia by distillation, which proves that nitrogen is not one of its elements. Gallic acid precipitates it from its solution; but the re-agent that most powerfully affects it is the sub-acetate of lead, which completely precipitates it from all its solutions. It appears, therefore, that emetin is a substance *sui generis*, possessing distinct and peculiar properties, which are the same from whatever plant it may have been obtained.

Pelletier and Dumas have since obtained the emetic principle of the *cæphelis emetica*, in a form so different from that above described, that it can scarcely be considered as the same substance. The decoction (it should appear) is to be mixed with pure magnesia, added in quantity sufficient not only to saturate the free acid, but to decompose the salt of which the emetic principle is the base. The liquid is to be decanted, and the sediment washed with cold water, then dried carefully, and digested in alcohol. To deprive it of all colour, it may be

united with an acid, treated with animal charcoal, again detached by magnesia, and redissolved in alcohol. By evaporation at a gentle heat, it is obtained white or yellowish, pulverulent, little soluble in cold water, but more so in hot, fusible at 122° Fahr., very soluble in alcohol; but not sensibly so in ether or in oils. It exhibits in a high degree an alkaline re-action, and saturates acids, without however giving crystallizable salts. It has no action on sub-acetate of lead, which is abundantly precipitated by the coloured substance above described, and its effects on the animal system were found to be produced in an equal degree in one-third the quantity. Its analysis gave

Carbon .....	64.57
Azote .....	4.
Hydrogen .....	7.77
Oxygen .....	22.95
	99.29

A bitter acrid principle, possessing emetic properties, has been extracted by Boullay from the *viola odorata*, but its chemical properties have not been fully detailed. (Quart. Journ. xvii. 335.) Vauquelin has extracted emetine also from the *ipeca-cuanha branca*, but only in small quantity.

*Sarcocoll.*—This substance is the spontaneous exudation of the *Pænea sarcocolla*, a plant which is a native of Ethiopia. It is brought over in small pieces, which are about the size of peas, and which are either of a pale red, or yellowish white colour.

Sarcocoll dissolves in the mouth like gum, and has a sweetish taste, after which there remains an impression of bitterness. It is soluble both in water and alcohol, and a strong solution of it forms a mucilage, which may be used for the purpose of a cement. Its most remarkable property is, that its solution is precipitated by tan, which distinguishes it sufficiently from gum. The substance most nearly approaching to it in chemical characters, is liquorice, the saccharine matter of which has a near resemblance to sarcocoll. (See Robiquet, Ann. de Chim. lxxii. and Thomson's Chemistry, iv. 31.)

*Olivile* is a name given by M. Pelletier to the substance, which remains after gently evaporating the alcoholic solution of the gum, which exudes from the olive tree. It is a white brilliant starchy powder, and sometimes it forms flattened needles.

It has no smell, but its taste is a mixture of bitter and sweet with something aromatic. It melts at  $158^{\circ}$ , and, on cooling, resembles a slightly yellowish transparent resin. Cold water scarcely acts upon it, but hot water dissolves 1-32d. It dissolves readily in alcohol, but not in ether or in volatile oils. Nitric acid dissolves it with heat, acquires a red colour, but becomes yellow on cooling, and deposits oxalic acid. Acetate of lead precipitates its aqueous solution, in flakes which are soluble in acetic acid. (Ann. of Phil. xii. 33.)

*Medullin* is a name given by Dr. John to the pith of the sun-flower (*Helianthus annuus*). It is destitute of taste and smell; insoluble in water, ether, alcohol, and oils, but soluble in nitric acid, which converts it into oxalic acid; and, when decomposed by destructive distillation, it leaves charcoal, having a metallic lustre like bronze. (Thomson's Chem. iv. 180.)

*Lupulin*.—This name has been given by Dr. Ives, not to any distinct vegetable principle extracted by chemical means, but to an impalpable yellow powder, in which he believes the virtue of the hop to reside, and which may be obtained by beating and sifting hops, of the kind used in brewing.

It appears to be peculiar to the female plant, and is probably secreted by the nectaries. In preserving beer from the acetous fermentation, and in communicating an agreeable flavour to it, lupulin was found to be equivalent to ten times its weight of hop leaves. It is itself a compound substance, consisting of tan, extract, a bitter principle, wax, resin, and lignin. If analyzed by the methods of Pelletier and Caventou, it is not improbable that an ingredient might be discovered, in the hop, of an alkaline nature, in which its narcotic virtue would be found to reside. (See Ann. of Phil. N.S. i. 194.)

*Cathartine*.—In examining the leaves of senna, Lassaigne and Fenuelle obtained a peculiar substance; to which, on account of its acting as a brisk purgative in very small doses, they gave the name of cathartine. A strained decoction of the leaves was precipitated by subacetate of lead, the precipitate washed and diffused through water, and then decomposed by sulphureted hydrogen. The liquor was filtered, evaporated to dryness, digested in alcohol, and the latter solution evaporated to dryness also. It contained acetate of potassa, which was decomposed by adding alcohol acidulated with a little sulphuric acid; the sulphate of potassa was separated by filtering, and the

excess of sulphuric acid separated by acetate of lead. Sulphureted hydrogen was again passed through the liquid, which, when filtered and again evaporated, gave the substance which they have called cathartine. It had a reddish colour, a peculiar smell, and a bitter nauseous taste; it dissolved in alcohol and water in all proportions, but was insoluble in ether. It became moist by exposure to the air. (Ann. de Ch. et Ph. xvi. 16.)

*Colocytine*.—The alcoholic solution of colocynth was found by Vauquelin to yield a very brittle substance of a gold yellow colour, partly soluble in water. The aqueous solution, when heated, becomes turbid, and yellow drops form both on its surface and bottom, resembling a fused resin, which, when cold, become hard and brittle. This bitter resin-like substance is slightly soluble in water; considerably so in alcohol and in alkaline solutions; and abundantly precipitated by infusion of galls, but not by acetate of lead. It contains the bitterness of the colocynth, and appears to M. Vauquelin to be a particular principle, for which he proposes the name of *colocytine*. (Quart. Journ. xviii. 400.)

*Rhéine*.—By acting, at a gentle heat, upon one part of powdered rhubarb with eight parts of nitric acid, sp. gr. 1.375, evaporating to the consistency of syrup, and then diluting with water, a peculiar precipitate falls, to which Vaudin has given the name of *rhéine*, from *rheum*, the Linnean name of rhubarb. When dried, this substance has an orange colour; is without any particular odour; has a slightly bitter taste; is soluble in water, ether, and alcohol, giving solutions which become yellow with acids, and of a rose red with alkalis. Ether extracts from rhubarb a similar substance, a proof that it exists in the plant ready formed, and is not the product of the action of nitric acid. (34 Ann. de Ch. et de Ph. 200.)

*Zanthopicrite* was extracted by Chevallier and Pelletier from the bark of a species of *Zanthoxilum*. It forms groups of greenish yellow crystals, in silky divergent needles, soluble in water and in alcohol, but not in ether. Its distinguishing property seems to be, that a solution of gold gives with it a precipitate which is quite soluble in alcohol and in liquid ammonia. (Ann. de Ch. et de Ph. Feb. 1827.)

*Conine*.—MM. Brande and Geiseke are said to have extracted an active principle from hemlock (*Conium maculatum*), half a grain of which proved fatal to a rabbit. A short notice respect-

ing it may be found in the Quart. Journ. April 1828. (See also Ann. of Phil. Nov. 1827.)

*Dracine*.—The gummi-resinous substance, called *dragon's blood*, has been examined by M. Melandri, and found to contain neither tannin nor gallic acid. A portion was dissolved in strong alcohol, evaporated till much concentrated, and poured into cold water, which precipitated a spongy mass. This, after being well washed with pure water, was covered with water containing  $\frac{1}{100}$ th of sulphuric acid, which at 61° Fahr. acted sensibly upon it. The residue, after being well washed with cold water, was of a fine red colour, was tasteless, inodorous, flexible, and fused at 131° Fahr. This substance, *dracine*, has some analogy, though but slight, with vegetable alkalis. The sulphate is obtainable by adding sulphuric acid diluted with alcohol to an alcoholic solution of dracine, precipitating by cold water, and then applying a gentle heat. The sulphate of dracine collects at the bottom, and is to be washed with cold water, till the washings cease to redden litmus paper. It is then to be dissolved in hot water. The solution is reddened by the smallest addition of alkalis, and is a most sensible test of their presence; it is also a delicate test of acids, which turn it yellow. The minutest quantity of carbonate of lime, contained in filtering paper, instantly converts the yellow colour of the solution to red. (Ann. of Phil. Nov. 1827.)

*Jalapine*.—M. Pelletier has examined this supposed principle from jalap, and finds it be nothing more than sulphates of lime and ammonia. (Phil. Mag. Dec. 1827, p. 462.)

*Piperine* has been extracted by M. Pelletier from black pepper, by digesting it in alcohol, and evaporating the solution, which left a fatty resinous matter. This, after being washed in warm water, was of a green colour, and had a hot burning taste. It dissolved readily in alcohol, and less readily in sulphuric ether, and the solution by heated alcohol, when left for some days, deposited a number of small crystals. These, being purified by repeated solutions and crystallizations, gradually lost their taste of pepper, which accumulated in the uncrystallizable fatty matter. The crystals of piperine were four-sided prisms; they were almost tasteless; were insoluble in cold and sparingly soluble in hot water; were very soluble in alcohol, and less so in ether; soluble in acetic acid, from which they

separated in feathery crystals. Weak acids did not dissolve, and strong acids decomposed them. Sulphuric acid acquired, by being heated with them, a blood-red colour, which disappeared on dilution. They fused at  $212^{\circ}$ , and, when decomposed by peroxide of copper, gave only water and carbonic acid.

In addition to piperine, M. Pelletier detected in pepper an acrid fixed oil; a volatile oil; a coloured gummy matter; extract, starch, and several other known vegetable principles. (*Ann. de Chim. et de Phys.* xvi. 337.)



## CHAPTER XI.

RESULT OF THE SPONTANEOUS DECOMPOSITION OF  
VEGETABLE SUBSTANCES.

## SECTION I.

*Vinous Fermentation.*

THE phenomena and results of the vinous fermentation may be accurately examined, by means of an apparatus similar to that which is described in Lavoisier's Elements, part iii. ch. vi. A more simple one, however, will sufficiently answer the purpose. It may consist of a large glass matras, shaped like fig. 4, capable of holding 10 or 12 pints. Into the opening of this matras, one leg of a glass tube, which has been twice bent at right angles, or into the form of a syphon, may be fixed by means of a perforated cork and cement. The aperture of the other leg of the syphon may terminate in a two-necked bottle, from which a bent glass tube is to proceed, and to be carried under the shelf of the pneumatic trough, or (which is better) into the receiving-pipe of a gazometer, fig. 35, *b*. The matras may then be half filled with a solution of sugar in four or five times its weight of water, or with an infusion of malt; and in either case a little yeast must be added. The juices of some plants, of the grape for instance, do not require the addition of yeast, but ferment spontaneously. It is probable, therefore, that they contain some principle that serves the purpose of yeast, in exciting the fermentative process.

When the vessel is placed in a room, the temperature of which is not below 60° Fahr. the fermentation soon begins to take place; a brisk motion is observed in the liquid; it becomes turbid, and deposits some impurities, while a frothy scum rises to the surface. When the materials are in large quantity, *viz.* sufficient to fill a cask, a hissing noise is heard in the liquid, and its bulk increases so much, that, if the vessel were full, it soon begins to overflow. At the same time, an immense quan-

tity of gas escapes, and passes, through the bent tube, into the receiver, which is inverted in the pneumatic trough, or into the gazometer. During the process of fermentation, the liquor preserves a higher temperature than that of the surrounding atmosphere. After some days, these appearances gradually subside; and, if the process has been well conducted, and suspended at the proper period, the result is a clear transparent liquor, not sweet, like that submitted to experiment, but having a vinous taste and smell, and the intoxicating powers of a fermented liquor. At the bottom is deposited a white matter, equal to about half the weight of the yeast, and giving, by analysis, oxygen, hydrogen, and carbon only, whereas the yeast itself affords azote also. Other azotized substances serve, too, the purposes of ferments, such as urine, soft cheese, gluten mixed with bitartrate of potassa, and coagulated albumen. These ferments, Colin is of opinion, are rendered more active by certain electrical states of the atmosphere; and, on the contrary, are rendered less efficient by the gradual development of alcohol, which takes place during fermentation.

When the gas contained in the gazometer is examined, it is found to be carbonic acid, holding in solution a portion of alcohol, not worth collecting, which gives it an odour like that of the fermented liquor. On submitting the liquor to distillation, we obtain a fluid considerably lighter than water, and having a strong spirituous taste. By the temperature of the vapour, which rises at different periods of distillation, it has been shown, by M. Groening, that it is easy to ascertain the strength of the spirit which is coming over at the time. (Ann. of Phil. N. S. iv. 396, and v. 313.)

#### *Panary Fermentation.*

The difficulty of classing the fermentation which takes place in dough, under any of the three kinds of the vinous, acetous, and putrefactive, led chemists to the conception that it was a kind of decomposition *sui generis*, which the above name was intended to designate. Dr. Colquhoun, in an ingenious memoir published in the Ann. of Philosophy, Sept. and Oct. 1826, has maintained the opinion that the sugar contained in all flour, to the amount of about 5 per cent. of its weight, is the exclusive subject of that process; and that the starch and gluten do not necessarily undergo any change in the fermenta-

tion of dough. The conversion, then, of sugar into alcohol and carbonic acid, is the essential part of the panary process; and the escape of those volatile products, in the oven, leaves the bread full of little cells or vesicles. After baking, bread is found to contain as much gluten as the original flour; and, of the starch, three-fourths remain unaltered, while one-fourth is converted into a gummy saccharine matter, which replaces the sugar destroyed by the fermentation. The production of any other acid, than the carbonic, does not take place, unless the dough is allowed to work beyond the proper time, and then a second decomposition of a different kind ensues, by which acetic acid is produced, and the quality of the bread is deteriorated. The art of the baker chiefly consists in checking the fermentation of the dough at the right period, by committing it to the oven when the first process is fully completed, and the second has not begun. No skill on his part will, however, supply the want of good materials; for if the flour or yeast has been originally of bad quality, the loaf will be sad or ill-raised, and even sour to the taste and smell. This imperfection may be abated by the use of a due proportion of carbonate of soda or ammonia, or carbonate of magnesia, intimately mixed, and then kneaded with the flour, without rendering the bread in any degree ill-flavoured, or injurious to the animal system. By supplying carbonic acid, the carbonates even contribute to render the bread lighter, and more palatable and wholesome.

This theory of the panary fermentation required only, for its full establishment, a fact which has been since ascertained by Mr. Graham of Edinburgh. He has actually, by inclosing a loaf in a distilling apparatus, and subjecting it to a baking temperature, obtained alcohol, of sufficient strength to fire gunpowder by its combustion, and varying in quantity from 0.3 to 1 per cent. of the weight of the flour employed. (Ann. of Phil. 2d Ser. xii. 363.)

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It is from fermented liquors that all the varieties of spirits, known under the names of brandy, rum, spirits of wine, arrack, gin, and whisky, are obtained; and they differ from each other merely in strength and flavour, the latter quality depending, probably, on a fine essential oil peculiar to each species. Essentially, they all consist of the same ingredient, which, when deprived of the water with which it is combined, is called *alcohol*.

## SECTION II.

*Alcohol.*

It had been a subject of controversy whether the alcohol, obtained by the distillation of wines, and of other fermented liquors, exists *ready formed* in those liquors, or is actually *generated*, in consequence of a new arrangement of the elements of the fluid, by the increased temperature at which the distillation is carried on. The latter opinion was supported by Fabroni (Ann. de Chim. xxx. 220), and had gained considerable currency, when it was set aside by Mr. Brande in two memoirs; in the first of which it was shown, that the quantity of alcohol, resulting from the distillation of wine, is neither increased nor diminished by a variation of temperature equal to 20 degrees of Fahr.; and in the second that alcohol may be obtained from fermented liquors, without the intervention of heat, by processes in which nothing more can be effected than the separation of water. (Phil. Trans. 1811, 1813.)

1stly. When a solution of acetate of lead (sugar of lead), or of subacetate of lead (Goulard's Extract), is added to wine, a dense insoluble precipitate is quickly formed, consisting of a compound of the metallic oxide, with the acid and extractive colouring matter of the wine. On filtering the fluid, we obtain a mixture of alcohol, water, and a portion of the acid of the metallic salt, provided the latter has not been added in excess, in which case a part of the salt remains undecomposed. From this liquid, hot and dry subcarbonate of potassa separates the water; and the alcohol floats at the top, forming a distinct stratum. By operating on artificial mixtures of alcohol and water, Mr. Brande found that when the alcohol is not less than 16 per cent. the quantity, indicated by the subcarbonate, was always within one half part in 100 of the real proportion contained in the mixture. The experiment may be performed in a glass tube, from half an inch to two inches diameter, accurately graduated into 100 parts.

2dly. To ascertain in a more simple way the quantity of alcohol in any wine, its acid may be saturated with potassa, and a given measure then distilled with a gentle heat nearly to dryness; the deficient bulk of the distilled liquor being made up with distilled water. This mixture is to be shaken, and set

aside for 24 hours. Its specific gravity will then show the quantity of alcohol which the wine contains, and this may be immediately seen by referring to Mr. Gilpin's Table, an abstract of which will be given in this section.

3dly. Gay Lussac recommended the substitution of very finely powdered litharge for the acetate of lead; and showed that wine distilled *in vacuo*, at the temperature of 60° Fahr. affords alcohol; a demonstrative proof that the alcohol obtained is merely *separated*, and not *formed*, by the process of distillation. (86 Ann. de Chim. 175.) This discovery has been applied to practice; and it has been found that spirits, distilled at a low temperature *in vacuo*, are of superior flavour to those procured by a distillation conducted in the ordinary manner.

From an extensive series of experiments, Mr. Brande has constructed the following Table. (Manual of Pharmacy, p. 167.)

*Table of the Quantity of Alcohol, of specific gravity .825 at 60° Fahr. in various Wines, &c.*

		Proportion of Spirit per cent. by measure.			Proportion of Spirit per cent. by measure.
1.	Lissa	26,47	7.	Sherry	19,81
	Ditto	24,35		Ditto	19,83
	Average	25,41		Ditto	18,79
2.	Raisin wine	26,40		Ditto	18,25
	Ditto	25,77		Average	19,17
	Ditto	23,20	8.	Teneriffe	19,79
	Average	25,12	9.	Colares	19,75
3.	Marsala	26,03	10.	Lachryma Christi	19,70
	Ditto	25,05	11.	Constantia, white	19,75
	Average	25,09	12.	Ditto, red	18,92
4.	Port	25,83	13.	Lisbon	18,94
	Ditto	24,29	14.	Malaga (1666)	18,94
	Ditto	23,71	15.	Bucellas	18,49
	Ditto	23,39	16.	Red Madeira	22,30
	Ditto	22,30		Ditto	18,40
	Ditto	21,40		Average	20,35
	Ditto	19,00	17.	Cape Muschat	18,25
	Genuine	16,00	18.	Cape Madeira	22,94
	Average	22,96		Ditto	20,50
5.	Madeira	24,42		Ditto	18,11
	Ditto	23,93		Average	20,51
	Ditto (Sercial)	21,40	19.	Grape wine	18,11
	Ditto	19,24	20.	Calcavella	19,20
	Average	22,27		Ditto	18,10
6.	Currant wine	20,55		Average	18,65

## Table continued.

	Proportion of Spirit per cent. by measure.		Proportion of Spirit per cent. by measure.
21. Vidonia . . . . .	19,25	38. Red Hermitage ..	12,32
22. Alba Flora . . . . .	17,26	39. Vin de Grave ....	13,94
23. Malaga . . . . .	17,26	Ditto . . . . .	12,80
24. White Hermitage	17,43	Average	13,37
25. Rousillon . . . . .	19,00	40. Frontignac . . . . .	12,79
Ditto . . . . .	17,26	41. Côte Rotie . . . . .	12,32
Average	18,13	42. Gooseberry wine ..	11,84
26. Claret . . . . .	17,11	43. Orange wine—ave-	
Ditto . . . . .	16,32	rage of six sam-	
Ditto . . . . .	14,08	ples made by a	
Ditto . . . . .	12,91	London manu-	
Average	15,10	facturer . . . . .	11,26
27. Malmsey Madeira	16,40	44. Tokay . . . . .	9,83
28. Lunel . . . . .	15,52	45. Elder wine . . . . .	8,79
29. Sheraz . . . . .	15,52	46. Cider, highest ave-	
30. Syracuse . . . . .	15,28	rage . . . . .	9,87
31. Sauterne . . . . .	14,22	Ditto, lowest ditto	5,21
32. Burgundy . . . . .	16,60	47. Perry, average of	
Ditto . . . . .	15,22	four samples ..	7,26
Ditto . . . . .	14,53	48. Mead . . . . .	7,32
Ditto . . . . .	11,95	49. Ale (Burton) ....	8,88
Average	14,57	Ditto (Edinburgh)	6,20
33. Hock . . . . .	14,37	Ditto (Dorchester)	5,56
Ditto . . . . .	13,00	Average	6,87
Ditto (old in cask)	8,88	50. Brown stout . . . .	6,80
Very old . . . . .	16,00	51. London porter(ave-	
Average	12,08	rage . . . . .	4,20
34. Nice . . . . .	14,63	52. Ditto small beer	
35. Barsac . . . . .	13,86	(ditto) . . . . .	1,28
36. Tent . . . . .	13,30	53. Brandy . . . . .	53,39
37. Champagne (still)	13,80	54. Rum . . . . .	53,68
Ditto (sparkling)	12,80	55. Gin . . . . .	51,60
Ditto (red) . . . . .	12,56	56. Scotch whiskey ..	54,32
Ditto (ditto) . . . .	11,30	57. Irish ditto . . . . .	53,90
Average	12,61		

Doubts have been excited of the accuracy of this Table, by a reference to the comparative intoxicating effects of port wine and brandy, the latter of which certainly are more than double those of the former. But it is to be considered that, in wine, the alcohol is in a state of combination with several other ingredients, which must necessarily diminish its activity on the animal system. In each kind of wine, deviations from the above proportions may, however, be expected to arise from the variable

purity of the liquors that may be the subjects of experiment. In Mr. Brande's analyses, great pains were taken to employ such wines as were perfectly unadulterated.

Differences must exist also in wines, arising from the various kinds and proportions of acid present in them. Wine from grapes contains no acid but tartaric in the state of bi-tartrate of potassa, which, on standing either in the cask or bottle, is gradually deposited. But the wine of other fruits, as the gooseberry, currant, &c. holds malic and citric acids in solution, which are not deposited, however long they may be kept, and are rendered palatable by an excess of sugar. It is owing to this excess of sugar, that the latter class of wines continue to ferment when bottled, and the carbonic acid, which is evolved, renders them brisk and foaming. Ale and beer contain, beside much mucilaginous and extractive matter derived from the malt, a little free acid also, which disposes them to pass more decidedly to the acetous state. The bitter flavour of the hop covers that of the acid, and renders the liquor less prone to conversion into vinegar, than it would otherwise be.

#### *Preparation of Alcohol.*

To prepare alcohol, the spirit of wine of the shops may be employed. To any quantity contained in a glass vessel, the sub-carbonate of potassa, perfectly dry, and heated to about 300° Fahr. is to be added; the mixture is to be well shaken; the clear liquor decanted; and this is to be repeated as long as the alkali is moistened by the spirit. When enough has been employed, the next addition will fall to the bottom in a perfectly dry state. The dry chloride of calcium (fused muriate of lime) may be advantageously used as a substitute for alkali; but it appears doubtful whether a little ether is not produced by its action. Saussure, however, is of opinion that this is not the case with alcohol which has been only twice treated with chloride of calcium, of which he employed, at two operations, first a quantity equal to half the weight of the spirit of wine, and secondly an equal weight. When the chloride is no longer moistened on being added to the spirit, we may conclude that enough has been used. Two distinct strata will then be seen in the liquid, the solution of muriate of lime in water, at the bottom, and the alcohol at the top. The latter is to be decanted, or drawn off by a syphon, and then submitted to distillation at

a gentle heat, reserving only the portions which first pass over. Gay Lussac recommends quicklime or baryta, in preference to muriate of lime; and Dubuc advises the use of dry alumina, by which he brought alcohol to the specific gravity .817, without any risk of forming ether by the process. (86 Ann. de Chim. 314.) It has been found also that spirit of wine of sp. gr. .867, when inclosed in a bladder, and exposed for some time to the air, is converted into alcohol of sp. gr. 0.817, the water only escaping through the coats of the bladder. (Quart. Journ. viii. 381, and xviii. 180.) But a more elegant method of concentrating alcohol is that of Mr. Graham. It consists in placing a shallow vessel, containing coarse powdered quicklime, on the plate of an air-pump, and supporting over it a smaller vessel containing a few ounces of spirit of wine. Covering both with a low receiver, the air is exhausted till the alcohol begins to boil. But of the vapour which is raised, the lime absorbs only the aqueous part; and as water cannot remain in alcohol, except when pressed by an atmosphere of its own vapour, it continues to arise, while the alcohol is kept down by the pressure of alcoholic vapour. In about five days, alcohol is thus entirely dephlegmated. (Edinb. Phil. Trans. 1828.)

Alcohol is considerably lighter than water. The lightest that can be obtained, by simple distillation, from spirit of wine, has the specific gravity of .825, distilled water at 60° Fahr. being 1. By the intervention of substances which strongly attract water, Chaussier brought it to the specific gravity of .798; Gay Lussac to 0.79235 at 64°; and Lovitz and Saussure, jun. to .791 or .792 at 68° Fahr. = .796 at 60° Fahr. Alcohol of the specific gravity .820 still contains, according to Lovitz, about  $\frac{1}{10}$ th its weight of water, and when of specific gravity .917 at 60° Fahr. it consists of equal weights of alcohol, specific gravity .796, and water. By an act of parliament passed in 1762, the specific gravity of *proof spirit* at 60° was fixed at .916, but .920 may be considered as [nearer the standard now adopted for proof spirits in this country. The term *above proof* is used to denote a spirit lighter than this, and *under proof* one which contains a larger proportion of water. Rectified spirit is directed, by the London Pharmacopœia, to have the specific gravity of .835, but it is seldom sold lighter than .840.

The quantity of alcohol and water, in mixtures of different specific gravities, may be learned from Mr. Gilpin's copious



tables, of which the following is a brief abstract. His alcohol had the sp. gr. .825, and Chaussier's, .798. (Phil. Trans, 1794, or Nich. Journ. 4to. vol. 1.)

*Table showing the Specific Gravity of the Mixtures of Alcohol and Water.*

Centesimal Parts of the Mixture.	SPECIFIC GRAVITIES.	
	According to Chaussier.	According to Gilpin (last Table.)
Alcohol . . . . 100	0.7980	0.825
95	0.8165	0.83887
90	0.8340	0.85244
85	0.8485	0.86414
80	0.8620	0.87606
75	0.87525	0.88762
70	0.8880	0.89883
65	0.9005	0.90941
60	0.9120	0.91981
55	0.9230	0.92961
50	0.9334	0.93882
45	0.94265	0.94726
40	0.9514	0.95493
35	0.95865	0.96158
30	0.96535	0.96736
25	0.97035	0.97239
20	0.97605	0.97723
15	0.9815	0.98213
10	0.9866	0.98737
5	0.99335	0.99327
0	0.99835	1.00000

It is on many occasions useful to know the proportion of the strongest alcohol that has hitherto been obtained, in mixtures of alcohol and water of different specific gravities. This is shewn by the following Table, constructed by Lovitz. It is founded on a series of experiments in which alcohol of the sp. gr. .791 at 68° was mixed with various proportions of water; allowed to stand during 24 hours; and then examined for its sp. gr. at the temperature of 68°. The fourth column has been added by Dr. Thomson, to express the sp. gr. at 60°, the temperature commonly preferred in this country.

*Table of the Strength of Alcohol of various Densities.*

100 parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alcoh.	Wat.	at 68°.	at 60°.	Alcoh.	Wat.	at 68°.	at 60°.
100	—	791	796	61	39	889	893
99	1	794	798	60	40	892	896
98	2	797	801	59	41	894	898
97	3	800	804	58	42	896	900
96	4	803	807	57	43	899	903
95	5	805	809	56	44	901	904
94	6	808	812	55	45	903	906
93	7	811	815	54	46	905	908
92	8	813	817	53	47	907	910
91	9	816	820	52	48	909	912
90	10	818	822	51	49	912	915
89	11	821	825	50	50	914	917
88	12	823	827	49	51	917	920
87	13	826	830	48	52	919	922
86	14	828	832	47	53	921	924
85	15	831	835	46	54	923	926
84	16	834	838	45	55	925	928
83	17	836	840	44	56	927	930
82	18	839	843	43	57	930	933
81	19	842	846	42	58	932	935
80	20	844	848	41	59	934	937
79	21	847	851	40	60	936	939
78	22	849	853	39	61	938	941
77	23	851	855	38	62	940	943
76	24	853	857	37	63	942	945
75	25	856	860	36	64	944	947
74	26	859	863	35	65	946	949
73	27	861	865	34	66	948	951
72	28	863	867	33	67	950	953
71	29	866	870	32	68	952	955
70	30	868	871	31	69	954	957
69	31	870	874	30	70	956	958
68	32	872	875	29	71	957	960
67	33	875	879	28	72	959	962
66	34	877	880	27	73	961	963
65	35	880	883	26	74	963	965
64	36	882	886	25	75	965	967
63	37	885	889	24	76	966	968
62	38	887	891	23	77	968	970

*Table continued.*

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alcoh.	Wat.	at 68°.	at 60°.	Alcoh.	Wat.	at 68°.	at 60°.
22	78	970	972	10	90	987	
21	79	971	973	9	91	988	
20	80	973	974	8	92	989	
19	81	974	975	7	93	991	
18	82	976		6	94	992	
17	83	977		5	95	994	
16	84	978		4	96	995	
15	85	980		3	97	997	
14	86	981		2	98	998	
13	87	983		1	99	999	
12	88	985		—	100	1000	
11	89	986					

*Properties of Alcohol.*

Pure alcohol, when mixed with water, unites with it intimately; and caloric is evolved during the union. Equal measures of alcohol and water, each at 50° Fahrenheit, give by sudden admixture an elevation of nearly 20° of temperature; and equal measures of proof spirit and water occasion an increase of 9½°. The bulk of the resulting liquid is less than that of the two before admixture. Thus a pint of alcohol and a pint of water, when the mixture has cooled to the temperature of the atmosphere, falls considerably short of two pints.

This diminution of bulk is best shown by a contrivance of Dr. Marcet, represented inverted in the annexed sketch. It consists of a glass vessel, formed of two spherical bulbs connected together, and terminating in a tube about 12 inches long, which is hermetically sealed at the lower end. The upper bulb has a neck and ground stopper. The tube and lower bulb are first to be filled with water, and the upper bulb with alcohol. The stopper being put into its place, the instrument is to be inverted, as shown in the figure; when the two fluids will unite; heat will be evolved; and, on cooling



to their original temperature, an empty space will be seen in the tube. The same instrument may be employed to show the diminution of bulk in sulphuric acid, and in other fluids, by mixture with water.

An exception to this law is stated by Thenard (*Traité de Chim.* iii. 309) in alcohol of density 0.9707; for 5 parts of this alcohol, mixed with 5 of distilled water, give a mixture of sp. gr. 0.9835, which is less than the mean (0.9854) of the alcohol and water before mixture. Hence, in this case, there must have been a dilatation of volume.

Alcohol is extremely *volatile*, and produces considerable cold by its evaporation. When a thermometer, after being immersed in spirit of wine, is suspended in the air, the quicksilver sinks two or three degrees. By repeated dippings and exposures, and by blowing upon the bulb with a pair of bellows, Dr. Cullen caused the thermometer to sink from 44° to below the freezing point. It has been found that the degrees of cold, produced by the evaporation of spirits, are proportional to the strength of the spirits. Thus if a certain degree of cold be produced by water, and another degree by alcohol, a spirit of half strength will give a degree of cold just half way between the two. (*Quart. Journ.* x. 187.)

Alcohol is highly *inflammable*, and burns away with a blue flame, without leaving any residuum. The light emitted by its combustion is feeble; but considerable heat is evolved, and it is employed, therefore, as a source of temperature in a variety of chemical processes. During its combustion, carbonic acid is generated; no charcoal appears; and a quantity of water is produced which exceeds in weight the alcohol employed, in the proportion, according to Saussure, of 132 parts of water from 100 of alcohol. The flame of alcohol acquires a red colour from muriate of lime, a deep blood-red from the muriate of strontia, and a green tinge from boracic acid.

Alcohol is remarkably *expansible by heat*. Dividing the scale between the freezing and boiling points of water into two equal parts, Mr. De Luc has stated that alcohol expands 35 parts for the first 90°, and 45 parts for the second 90°. The strength of his alcohol, however, is described only by the indefinite test of its firing gunpowder. Mr. Dalton found that 1000 parts of alcohol, of the specific gravity .817, at 50° Fahrenheit, became 1079 parts at 170°. At 110°, half way between

the two extremes, the alcohol was at 1039, or half a division below the true mean. The more the alcohol was diluted with water, the greater he found the disproportion to be between the two parts of the scale. When of the specific gravity .967, answering to 75 per cent. water, the ratio of expansion through the first half between 50° and 170°, was to that through the second half as 35 to 45, which is precisely the same as De Luc gives for pure alcohol. In reporting these results, no account is taken of the expansion of the glass vessel, and consequently the real expansions may be considered as rather exceeding the apparent ones which have been stated.

Alcohol, sp. gr. .820, *boils* at 176°, or in vacuo at 56°. When of sp. gr. .800 its boiling point is 173.5. If water be added, its boiling point is raised. Alcohol, sp. gr. 0.900, Mr. Dalton finds to boil at 182° Fahr., of sp. gr. 850 at 170°. In this case, as in others where two volatile liquids are mixed, the boiling point is varied, but not proportionably; for the mixture boils nearest the boiling point of that which is most volatile. Thus a mixture of equal parts of alcohol, of such strength as to boil at 170°, and water, ought by the rule of proportion to boil at 194°, but in fact it boils at 183°. A Table of the boiling points of various mixtures of alcohol and water may be consulted in the Ann. of Phil. N. S. v. 313.

Alcohol of the specific gravity .8152 at 50° Fahr. *gives a gas*, the density of which is to that of the atmosphere as 1.613 to 1. According to Berzelius and Dulong, the density of the vapour of pure alcohol is 1.6004. (Ann. de Chim. et Phys. xv. 395.) Of the forces of vapour of alcohol at different temperatures, Dr. Ure has given a Table, (Phil. Trans. 1818) which will be copied into the Appendix. To become gaseous, alcohol absorbs only 0.436 of the caloric required to vaporize an equal weight of water.

Alcohol has never yet been *congealed* by any known method of producing artificial cold. Mr. Walker, of Oxford, found that it continued fluid at -91° Fahr. Even when diluted with an equal weight of water, it requires a cold of 6° below 0 to congeal it. Mr. Hutton, of Edinburgh, announced, indeed, several years ago, (Nich. Journ. xxxiv. 166) that he had succeeded in congealing alcohol of the sp. gr. 798, but no confirmation of the fact has yet been published.

Alcohol has no action whatsoever, at common temperatures, on hydrogen, oxygen, or azotic gases, on atmospheric air, nor on carbon or boron. Chlorine decomposes it, muriatic and carbonic acids being formed; a matter which has an oily appearance precipitates; and some carbon also appears in a free state. It dissolves iodine to a considerable extent; not however without a partial decomposition, and a formation of hydriodic acid.

Alcohol is a powerful *solvent*. It dissolves soap; vegetable extract; sugar; oxalic, camphoric, tartaric, gallic, and benzoic acids; volatile oils; fixed oils, sparingly, except castor oil, which it dissolves in considerable quantity; resins, and balsams. It combines, also, with sulphur, phosphorus, and the pure alkalis; but not with their carbonates, nor, when pure, with any of the earths. Of the class of salts with alkaline, earthy, and metallic bases, alcohol dissolves some copiously, others sparingly, and others not at all. The proportion, in which some of these are taken up, is stated in the following Table by Wenzel, the principal defect of which is the omission of the specific gravity of the alcohol employed.

Two hundred and forty grains of boiling alcohol dissolve of

	Grains.		Grains.
Borate of ammonia . . . .	1	Nitrate of magnesia . . . .	694
Fluate of alumina . . . .	1	———— potassa . . . .	5
———— ammonia . . . .	1	———— soda . . . . .	23
Muriate of ammonia ..	17	Oxalate of alumina . . . .	7
———— lime . . . . .	238	Tartrate of alumina . . . .	7
———— magnesia ..	1313	———— ammonia ..	7
———— potassa . . . .	5	———— potassa . . . .	1
Nitrate of alumina . . . .	240	Super-tartrate of potassa	7
———— ammonia ..	214	———— oxalate of potassa	7
———— lime . . . . .	388		

Mr. Kirwan, also, has given a very useful Table, showing the power of alcohol, at different specific gravities, to dissolve several of the neutral salts. The salts were first deprived of their water of crystallization, and were digested, during three days, with alcohol, the temperature of which never exceeded 80° Fahrenheit.

	100 Grains of Alcohol at				
	.900	.872	.848	.834	.817
Sulphate of soda . . . . .	0	0	0	0	0
———— magnesia . . . . .	1	1	0	0	0
Nitrate of potassa . . . . .	2.76	1	0	0	0
———— soda . . . . .	10.5	6	....	0.38	0
Muriate of potassa . . . . .	4.62	1.66	....	0.38	0
———— soda . . . . .	5.8	3.67	....	0.5	
———— ammonia . . . . .	7.5	4.75	....	1.5	
———— magnesia . . . . .	21.25	....	23.75	36.25	50
———— baryta . . . . .	1	....	0.29	0.18	0.09
———— crystallized . . . . .	1.56	....	0.43	0.32	0.06
Acetate of lime . . . . .	2.4	....	4.12	4.75	4.88

Some salts, when actually dissolved in water, are precipitated by the addition of alcohol. This is the case chiefly with the sulphates, several of which are precipitated immediately, while others are not separated without the application of heat, nor till after a few days' repose.

It has been discovered by Mr. Graham of Edinburgh, that alcohol is capable of forming, with certain bodies, chiefly salts, compounds analogous to hydrates, which may be called *alco-hates*. They can only of course be obtained with such bases, as are soluble in alcohol, and the bases should be first deprived of water, and then be dissolved in absolute alcohol with the assistance of heat. On cooling, *alco-hates* are deposited, generally in confused crystals, but in some cases of a distinct crystalline form. The crystals are soft, transparent, and easily fusible by heat in their *alcohol of crystallization*, the proportion of which is generally considerable. In some of these compounds, the alcohol is retained by an affinity, which is not overcome by a temperature of 400° or 500° Fahr., and the alcohol is in atomic proportion. The *alco-hates*, already known, are those of chloride of calcium, nitrate of magnesia, nitrate of lime, proto-chloride of manganese, and chloride of zinc. (Qt. Jn. of Sc. N. S. Dec. 1828.)

Potassium and sodium, when brought into contact with hol, rectified as highly as possible, pass to the state of potassa and soda by absorbing oxygen. At the same time, hydrogen gas is evolved, a sufficient proof that the elements of water are present in the purest alcohol.

When the suboxide of platinum, prepared according to the process of Mr. E. Davy, or the sulphureted oxide of that metal precipitated from its solution by sulphureted hydrogen, is

moistened with alcohol, the alcohol is converted, at the expense of the oxygen of the atmosphere, into acetic acid and water. (Döbereiner in *Ann. de Ch. et de Ph.* xxiv. 91.)

Alcohol, when transmitted through a red-hot copper tube, is decomposed. The tube is found lined with a very fine light soot resembling lamp-black, and an enormous quantity of carburated hydrogen gas is evolved, not less, as appears from an experiment of Van Marum, than ten cubic feet, by the decomposition of three ounces of alcohol.

*Composition of Alcohol.*—To determine the composition of alcohol, Lavoisier burned a quantity, with very minute attention to the products, by means of an apparatus described in his *Elements of Chemistry*, Part III. ch. viii. sect 5; but as he has not stated the sp. gr. of his alcohol, his results are deprived of much of their value.

Saussure jun. in an elaborate series of experiments on the composition of alcohol, (*Nich. Journ.* xxi.; or *Ann. de Ch.* lxxxix.) employed several different methods; but that on which he placed most reliance, was a careful analysis of the products, obtained by transmitting alcohol through a red-hot porcelain tube. According to these experiments, alcohol, sp. gr. 0.792 at 68°, consists of

Carbon .....	51.98
Oxygen .....	34.32
Hydrogen .....	13.70
	100.

The atomic constitution most nearly agreeing with this statement, is the following :

Carbon ....	2 atoms	....	12	.....	52.17
Oxygen ....	1 do.	....	8	.....	34.79
Hydrogen ..	3 do.	....	3	.....	13.04
			23		100.

The accuracy of Saussure's experiments has been fully confirmed by Dumas and Boullay, who carefully analyzed alcohol by transmitting it over ignited peroxide of copper. (*Ann. de Ch. et de Ph.* Nov. 1827.) There can be little doubt, then, that the true constitution of alcohol is that above stated. But in order to compare its composition with that of ether, as we shall soon have occasion to do, it will be found more convenient to double those numbers, and to consider alcohol as represented by



Carbon	.....	4 atoms	.....	24
Oxygen	.....	2 do.	.....	16
Hydrogen	....	6 do.	.....	6
				46

Two atoms of oxygen are probably associated with two atoms of hydrogen, composing two atoms of water. The remaining four atoms of hydrogen with four atoms of carbon, form two atoms of olefiant gas. We may consider alcohol, then, under another aspect, as constituted of

Olefiant gas	....	2 atoms	....	14 × 2 = 28	....	100.
Aqueous vapour	.	2 atoms	....	9 × 2 = 18	....	64.29
				46		
Weight of the atom of alcohol	.....					46

To reduce the combining weights to volumes, we have only to divide the actual weights of olefiant gas and aqueous vapour, present in alcohol, by their respective densities, which gives their volumes. Thus,

$$100. \div .9722 \text{ (density of olefiant gas)} = 102.75 \text{ vols.}$$

$$64.29 \div .625 \text{ (density of aq. vapour)} = 102.86 \text{ vols.}$$

Hence it appears that alcohol is constituted of 102.75 volumes of olefiant gas + 102.86 volumes of aqueous vapour, proportions so nearly equal, that we may admit alcohol to consist of precisely equal volumes of olefiant gas and aqueous vapour. To determine the state of condensation in which these elements exist, it is necessary to compare the density of the vapour of alcohol, as determined by experiment, with that which would result from theory. Now, the density of the vapour of alcohol, ascertained by Gay Lussac, is 1.613; and on the supposition that the condensation of the elements of alcohol is half the sum of their united volumes, we obtain .9722 + .625 = 1.599; a coincidence as near as can reasonably be expected.

In order to understand the theory of the production of alcohol, which has been proposed by Gay Lussac, it is necessary to recapitulate the results of the analysis of sugar, made by that philosopher in conjunction with Thenard; *viz.*

Sugar = {	Charcoal	42.47
	Oxygen and hydrogen in the proportions required to form water	57.53
		100.00

Or of 102 volumes of gaseous carbon + 92 volumes of aqueous vapour. The composition of sugar, however, as will appear by reference to the table, page 218 of this volume, is so variable, that we may be allowed to consider it, on an average, as composed of 40 parts by weight of charcoal and 60 of water. Converting these weights into volumes, we shall have

$$\text{Sugar} = \begin{cases} 1 \text{ volume of gaseous carbon,} \\ 1 \text{ volume of aqueous vapour :} \end{cases}$$

or

$$\text{Sugar} = \begin{cases} 1 \text{ volume of gaseous carbon,} \\ 1 \text{ volume of hydrogen,} \\ \frac{1}{2} \text{ a volume of oxygen.} \end{cases}$$

But alcohol, it has been already stated, is constituted of

$$1 \text{ vol. of olefiant gas} = \begin{cases} 2 \text{ vols. gaseous carbon,} \\ 2 \text{ vols. hydrogen.} \end{cases}$$

$$1 \text{ vol. aqueous vapour} = \begin{cases} 1 \text{ vol. hydrogen,} \\ \frac{1}{2} \text{ vol. oxygen :} \end{cases}$$

or

$$\text{Alcohol} = \begin{cases} 2 \text{ vols. of gaseous carbon,} \\ 3 \text{ vols. hydrogen,} \\ \frac{1}{2} \text{ a volume of oxygen.} \end{cases}$$

And tripling the numbers representing the elements of sugar, in order to equalize the hydrogen of both,

$$\text{Sugar} = \begin{cases} 3 \text{ vols. of gaseous carbon,} \\ 3 \text{ vols. hydrogen,} \\ 3 \text{ half volumes of oxygen.} \end{cases}$$

Comparing, then, the composition of sugar with that of alcohol, it follows that to transform sugar into alcohol, we must remove

$$\begin{aligned} & 1 \text{ vol. of gaseous carbon,} \\ & 1 \text{ vol. of oxygen gas,} \end{aligned}$$

which, by combining, form 1 volume of carbonic acid, and leave 2 vols. of gaseous carbon, 3 vols. of hydrogen, and one half vol. of oxygen, to constitute alcohol. Reducing these volumes to weights, 100 pounds of sugar should afford 51.34 of alcohol and 48.66 of carbonic acid. (Gay Lussac, 95 Ann. de Chim. 311.)

## SECTION III.

*Ethers in general.*

By acting upon alcohol with almost any acid, that fluid undergoes a change, by which it loses its original properties, and is converted into ether. Sulphuric acid was first applied to this purpose, and the ether produced by its intervention was for a long time the only one that was known. Others have been since discovered, sufficiently numerous to render it, in the opinion of some chemists, desirable to arrange the ethers into classes. Boullay sen. divides them into three; 1st. those obtained by acting upon alcohol with sulphuric, phosphoric, and arsenic acids, which are all identical; 2dly. those produced by the combination of hydro-carbon with certain hydracids; 3dly. those which, according to the experience of Thenard and of Boullay, are constituted of alcohol and an oxid. As sulphuric ether is the one most generally known, and as it constitutes, according to the views of Dumas and Boullay jun., the base of certain others, I shall consider it first in order.

*Preparation of Sulphuric Ether.*

To prepare *sulphuric ether*, pour into a retort any quantity of alcohol, and add, at intervals, an equal weight of concentrated sulphuric acid, agitating them together each time, and taking care that the temperature of the mixture does not rise above 120° Fahr. Let the retort be placed in a sand-bath previously heated to 200° or upwards, and be connected, by means of an adopter, with a tubulated receiver. To the tubulure of the receiver, a glass tube twice bent at right angles may be luted; and its aperture be immersed in a cupful of water or mercury. The condensable vapour is thus confined; while the gases that are produced are allowed to escape. The receiver and adopter should be kept cool by the constant application of ice or of moistened cloths. As soon as the materials begin to boil, ether is produced, and passes over into the receiver. The ebullition is to be continued, till white vapours appear in the retort, or a smell of sulphurous acid is perceived; and the receiver is then to be removed. The liquor, which it contains, will probably have the sp. gr. .78 or .79, and will emit a smell of sulphurous acid. To purify it, a small quantity of caustic potassa may be added, and the mixture may be kept in a bottle about 24 hours,

agitating it occasionally. The clear liquid is then to be decanted, and distilled in a water-bath, till one half has come over; the sp. gr. of which should be at most .75. This is to be preserved in a well-closed phial. Its weight will be, to that of the alcohol employed, as about 1 to 3. It may be further purified, and rendered specifically lighter, by the action of water, applied in a manner which will presently be described.

*Oil of wine.*—If, when the ether ceases to be formed, the receiver be removed, and the heat still continued, sulphurous acid is produced abundantly, and a yellowish liquor, very different from ether, distils over. This may be mixed with a small quantity of liquid potassa to correct the sulphurous smell, and then submitted to a heat sufficient to drive off the small proportion of ether. The *oil of wine* remains swimming on the watery liquid.

Oil of wine may be procured more abundantly, by distilling one measure of sulphuric acid with one measure of alcohol, and may be purified by agitating it with a weak solution of sub-carbonate of potassa. The liquid obtained has a fragrant smell, and a bitterish pungent flavour; its sp. gr. is 1.060; it does not mix with ether, but combines with alcohol; it has no reaction on the tests of acids.

According to Mr. Hennell, oil of wine is a compound of hydrogen and carbon (in the proportions constituting olefiant gas) with sulphuric acid, the latter being so intimately combined, as not to be discoverable by its appropriate tests. If to the oil of wine gently warmed, a solution of baryta be added, no apparent decomposition ensues; but if a portion of the fluid, to which a barytic solution has been added, be boiled to dryness, sulphate of baryta is then formed, equivalent to 37 or 38 grains of sulphuric acid from 100 grains of the ethereal oil. When potassa is added to the oil of wine, and the mixture evaporated, a salt precisely resembling sulpho-vinate of potassa is left, the constitution of which nearly approaches to 1 atom of potassa, 2 of sulphuric acid, 4 of carbon, and 4 of hydrogen.

Oil of wine was found by Mr. Hennell to contain a variable portion of hydro-carbon, exceeding that which is necessary to constitute sulpho-vinic acid. Of this, a part is spontaneously deposited, by keeping, in a crystalline form, and the part so deposited is resolved by analysis into an atom of carbon + an atom of hydrogen, the elements of hydro-carbon.

By agitating oil of wine with a sufficient quantity of water, with or without potassa, that portion of hydro-carbon, which exceeds what is necessary to constitute sulpho-vinic acid, is liberated in the form of an oil, of a bright amber colour, and a consistency resembling castor oil. This oil has an agreeable odour; the sp. gr. of about 0.9; it is insoluble in water, very soluble in ether, but somewhat less so in alcohol; and burns with a brilliant flame, throwing off some carbon. Its analysis by peroxide of copper gave, very nearly, 85.61 carbon + 13.11 hydrogen.

By the loss of one-half of its hydro-carbon, oil of wine is converted into sulpho-vinic acid. The power of this acid to saturate bases, is equivalent to one-half that of the sulphuric acid which it contains. The remaining half of the hydro-carbon enters, as an element of the new acid, into the saline compounds called *sulpho-vinates*, and in these is equivalent, in saturating power, to the quantity of base taken up; the proportions of hydro-carbon which in this way replaces bases, being 4, = 24 carbon + 4 hydrogen. (Phil. Trans. 1826, p. 240.)

MM. Dumas and Boullay account for these facts, by supposing that, in the production of oil of wine, hypo-sulphuric acid is formed; but they evidently operated on a different fluid, from that known in this country by the name of oil of wine, and their supposition has not been confirmed by the recent experiments of Sèrullas. The existence of an acid, having the characters of that originally pointed out by Dabit (Ann. de Ch. et de Ph. xiii.) and subsequently submitted to experiments by Vogel and other chemists, under the name of sulpho-vinic acid, appears to be sufficiently established. It has however been considered by Sèrullas as a bi-sulphate of ether, and when deprived of its excess of acid, or neutralized by an addition of carbon, it then constitutes what he regards as the neutral sulphate, or oil of wine. (Ann. de Ch. et de Ph. Oct. 1828.) But it appears to me that its combinations with alkaline and earthy bases, which are neutral salts having no analogy with sulphates, are more consistent with the opinion that the sulpho-vinic is a distinct acid.

#### *Properties of Sulphuric Ether.*

Sulphuric ether is perfectly limpid and colourless, its smell powerful and fragrant; and its taste hot and stimulating. Its refractive power is 5.197. When pure, it has no acid reaction, nor do the tests of sulphuric acid produce any effect on it.

Ether is extremely light, having the specific gravity of .713 (Dumas and Boullay, jun.), or, according to Lovitz, even of .632. The specific gravity of ether, as found in the shops, is seldom less than .750, and generally heavier. It is in fact a mixture of ether and alcohol. The following Table has been constructed by Mr. Dalton from direct experiments on mixtures of ether, sp. gr. .720, with alcohol of sp. gr. .830.

*Table of the Specific Gravities of Mixtures of Ether and Alcohol.*

Ether.	Alcohol.	Sp. Gr.	Ether.	Alcohol.	Sp. Gr.				
100	+	0	.....	0.720	40	+	60	.....	0.792
90	+	10	.....	0.732	30	+	70	.....	0.804
80	+	20	.....	0.744	20	+	80	.....	0.816
70	+	30	.....	0.756	10	+	90	.....	0.828
60	+	40	.....	0.768	0	+	100	.....	0.830
50	+	50	.....	0.780					

From this Table, it should appear that the rectified ether of the London Pharmacopœia, sp. gr. 0.750, contains about 25 per cent. by weight of alcohol, and the unrectified ether from 55 to 60 of alcohol, the standard ether being reckoned as having the sp. gr. 720.

It has been observed by Girard, that rectified ether escapes through a capillary tube with much greater velocity than either water or alcohol, the relative times, for equal quantities of each fluid, being 101 seconds for ether, 349 for water, and 856 for alcohol. The comparative heights, to which these three fluids rose in the same capillary tube, were found to be nearly 6 for ether, 9 for alcohol, and 13 for water. (6 Ann. de Chim. et de Phys. 239.)

Ether does not, like alcohol, combine in a considerable proportion with water; and when the two fluids are shaken together, they mostly separate again on standing. Water, however, retains about one-tenth its weight of ether; and acquires an odour, which is much the same as that of ether itself. By repeated agitation with water, ether is deprived of most of the alcohol which it contains, is brought to a high degree of purity, and acquires the property of dissolving caoutchouc.

Ether is exceedingly volatile. A few drops, poured on the hand, evaporate instantly; and produce a sense of intense cold. By pouring a small stream of ether, from a capillary tube, on thermometer bulb filled with water, the water may be frozen

even in a warm summer atmosphere. Under the pressure of the atmosphere, ether of sp. gr. .713 boils at 93.2° Fahr. (Dumas and Boullay); and *in vacuo* at 20 degrees below 0. Two ounce-measures, converted into gas at the temperature of 72½° Fahr., fill the space of a cubic foot. (Saussure jun.) According to Gay Lussac, ether produces a gas, the density of which is to that of air, as 2.586 to 1. Berzelius and Dulong state its density to be 2.5808.

The elastic force of the vapour of ether may be beautifully shown by letting up a drop or two of sulphuric ether into the vacuum of a common barometer, when it will instantly depress the mercury several inches, more or less, according to the temperature. It is easy to know, in this way, what force the vapour of ether will at any time acquire in air, since its force is always just the same in air, as in a vacuum at a given temperature. Suppose its force *in vacuo*, when the barometer stands at 30, to be 10 inches, then  $\frac{30}{30 - 10} = 1.5$ ; that is, if ether be passed up into air under those circumstances, it will in due time increase the volume of air 50 per cent. This, however, is true only of pure ether, for if impure ether be passed through water, it is improved in quality, though diminished in quantity. (Dalton.) When gases, mingled with the vapour of ether, are confined by dry mercury, they may be kept over it, without sustaining any loss of ether. But such mixtures cannot be kept over alcohol, without sustaining a rapid loss of ethereal vapour. Over water, there is a loss also, but much less rapid.

The force of the vapour of ether, at different temperatures, has been investigated by Mr. Dalton and by Dr. Ure, but the results of the latter are objectionable, on account of the impurity of the ether which he employed. Mr. Dalton has given the following Table, showing the force of ethereal vapour at a few temperatures;

Temperatures in degrees of Fahr.	Force of Ethereal Vapour.
36° .....	7.5 inches.
64 .....	15.
96 .....	30.
132 .....	60.
173 .....	120.
220 .....	240.

The experiments, on which the foregoing Table is founded were not carried further than  $212^{\circ}$ ; but as that temperature gives a force of 207 or 209 inches, the force at  $220^{\circ}$  may be inferred to be 240 inches.

The boiling point of mixtures of ether and alcohol, Mr. Dalton found, may be made to vary from  $96^{\circ}$  to  $170^{\circ}$ ; but we cannot, from the proportions of any mixture, infer what will be the boiling point, which is always much nearer that of ether, than the proportions between the alcohol and ether would indicate.

A mixture of sulphuric and muriatic ethers evaporates instantaneously, and produces a degree of cold considerably below 0 of Fahrenheit.

Sulphuric ether assumes a solid form, by reducing its temperature to  $-46^{\circ}$  of Fahrenheit.

Ether does not dissolve the fixed alkalis, but it combines with ammonia. It dissolves essential oils and resins, and takes up about a twentieth of its weight of sulphur, which is deposited, sometimes in crystals, as the ether volatilizes. Ether dissolves, also, a small portion of phosphorus, and the solution, when poured on the surface of warm water in the dark, emits a lam-bent blue flame. This solution also, by very slow evaporation, affords crystals of phosphorus.

Sulphuric ether was observed by M. Planche to undergo a spontaneous change when kept in a vessel not entirely full, and frequently opened and exposed to the light. By this exposure, ether becomes acid in consequence of the production of vinegar, and loses somewhat of its sweet odour and its volatility. (*Ann. de Ch. et de Ph.* ii. 213.) This observation has been confirmed by Gay Lussac, who found that ether, which had been very attentively purified, so that its boiling point did not exceed  $96^{\circ}$  Fahr., nor its density 0.7119, and which had no action on turn-sole, acquired this last property by keeping, and at the same time became specifically heavier and less volatile. (*Ibid.* ii. 98.) When a part of the ether thus altered was distilled off, the residue evidently contained both acetic and sulphuric ether, and a peculiar kind of oil, which probably exists in all ether, since that fluid, even when recently and skilfully prepared, leaves an evident spot on the glass, on which a few drops are put to evaporate. M. Henry, of Paris, has since traced the acetic acid to the decomposition of acetic ether, which he has detected in all the sulphuric ether he has examined, however, carefully prepared. In proof



of this, he states that when iron, zinc, or any other oxidable metal, is kept in contact with sulphuric ether, after some time a notable portion of the acetate of that metal is discoverable in the liquid.

*Combustion of ether.*—The slow combustion of the vapour of ether is best shown by passing a few drops into a receiver furnished with a brass cap and stop-cock, to which a small pipe is screwed, and inverted in water of the temperature of  $100^{\circ}$ . The receiver will be filled with the gas of ether, which may be expelled through the pipe and set on fire. It burns with a beautiful deep blue flame.

Ether previously mixed with oxygen gas, constitutes a mixture which detonates loudly. Into a strong two-ounce phial, filled with oxygen gas, and wrapped round with a cloth, to secure the hand from injury, let fall a drop of ether. On applying the flame of a candle, a violent detonation will ensue. Or to a portion of oxygen gas, contained in the detonating tube, fig. 28, pass up a drop or two of ether. The volume of the gas, at temperatures from  $60^{\circ}$  to  $70^{\circ}$ , will be about doubled; below those temperatures it is less than doubled; and above, more than doubled. If doubled, or upwards, an electric spark will probably not occasion an explosion, owing to the excess of ethereal vapour. To produce a complete combustion, the ether vapour should be only from 3 to 10 per cent. of the volume of the oxygen, and the residue in that case consists of oxygen only. Ten volumes of ether vapour produce, according to Mr. Dalton, 40 volumes of carbonic acid, and consume 60 of oxygen. Atmospheric air does not form a combustible mixture, if the vapour exceed 5 per cent., and it rarely explodes with less than 2 per cent.

The vapour of ether explodes spontaneously with chlorine, as is shown by the following experiment, described by Mr. Cruickshank. (Nicholson's Journal, 4to. v. 205.) Fill a bottle, of the capacity of three or four pints, with chlorine gas, taking care to expel the water as completely as possible. Then throw into it about a dram or a dram and a half of good ether, covering its mouth immediately with a piece of light wood or paper. In a few seconds, white vapour will be seen moving circularly in the bottle, and this will soon be followed by an explosion, accompanied with flame. At the same time a considerable quantity of carbon will be deposited, and the bottle will be found to contain carbonic acid gas.

During his investigations on flame, Sir H. Davy discovered that, when a piece of fine platinum wire is heated and placed over the surface of ether in an open glass, a pale lambent flame plays around it, the wire becoming red, and even white hot, and frequently inflaming the ether. At the same time, peculiarly pungent fumes arise, the production of which takes place at all temperatures, from a heat rather above the boiling point of mercury, until the ether is inflamed. These vapours are extremely acrid and pungent; they resemble chlorine in smell; and affect the eyes in a manner similar to the compound of chlorine and nitrogen. Their nature was examined by Mr. Faraday. (Quart. Journ. of Science iii. 77.) By passing considerable quantities of a mixture of atmospheric air and ether through a heated glass tube, containing platinum in wire and leaf, he obtained a clear and colourless liquor, of a slightly acid taste and strong irritating smell. It reddened litmus paper, as did, also, its vapour. When heated, it was quickly dissipated, leaving on the capsule a slight coaly mark. It united to ammonia, and formed a neutral salt, which, by careful evaporation, might be obtained solid, but was volatile, even at temperatures below boiling water, producing a peculiar fetid smell. It united with potassa, and formed a salt, from which the acid was expelled by heat alone. The acid solution displaced carbonic acid from all the alkaline carbonates; and salts were obtained, from which the acid was again expelled by all the stronger acids. Mr. Daniell, also, having collected more than a pint and a half of this acid liquor, investigated its properties, and at first concluded that it was a new acid, which formed a distinct set of compounds with bases. He gave it, therefore, the name of *lampic acid*; and its compounds that of *lampates*. (Quart. Journ. vi.) Having since, however, been induced, by the near approach of its equivalent number to that of acetic acid, to resume its examination, he finds that the acid, formed during the slow combustion of ether, is merely the acetic, holding in solution some compound of carbon and hydrogen, which differs both from ether and alcohol. (Quart. Journ. xii.) It is to the presence of this compound, that lampic acid owes its property of precipitating gold, platinum, silver, and mercury, from their solutions in a metallic state; and of affording salts, which, in their forms and properties, differ somewhat from acetates formed with similar bases.

*Composition of Sulphuric Ether, and Theory of its Formation.*

By following the same processes, as those which have been already described in speaking of alcohol, and also by the rapid combustion of ether with oxygen gas, Saussure found that 100 parts of sulphuric ether, of specific gravity 0.7155 at 68° Fahr. contain

Carbon .....	67.98
Oxygen .....	17.62
Hydrogen .....	14.40
	100.

The analysis of sulphuric ether has been repeated with the greatest care by Dumas and Boullay, jun. The specific gravity of the fluid, on which they operated, was .713 at 68° Fahr. By transmission over ignited peroxide of copper, it was resolved into the following elements:

	By experiment.		By calculation.
Carbon .....	65.05	.....	64.96
Hydrogen .....	13.85	.....	13.47
Oxygen .....	21.24	.....	21.57
	100.14		100.00

Now the density of the vapour of sulphuric ether is, by experiment, 2.581; and if we suppose it to be constituted of two volumes of olefiant gas and one volume of aqueous vapour, and that the condensation is two-thirds of their united volume, we obtain 2.5694 for the density of ether-vapour. This would lead to the following view of the constitution of ether, which, from its coincidence with experiment, is probably the true one:

Olefiant gas .....	2 atoms .....	14 × 2 = 28
Aqueous vapour .....	1 atom .....	9
		37

Contrasting, then, the composition of alcohol and that of ether, it will be easy to perceive what takes place, when the former is converted into the latter.

Alcohol consists of		Ether consists of
Olefiant gas .....	2 atoms	Olefiant gas .....
Aqueous vapour .....	2 atoms	Aqueous vapour .....

Or, in volumes,	In volumes,
Olefiant gas . . . . 2 volumes	Olefiant gas . . . . . 2 volumes
Aqueous vapour .. 2 volumes	Aqueous vapour .. 1 volume

To change alcohol into ether, all that is necessary is to take away one atom, or one volume, of aqueous vapour; and in this removal of one-half the water, which forms an element of alcohol, it seems to be universally agreed, even among those who differ as to the precise number of atoms constituting those fluids, that etherification consists. If the conversion could be made without any loss, 46 parts of absolute alcohol should give 37 parts of ether, or 100 parts by weight of alcohol should give very nearly  $80\frac{1}{2}$  of ether, a proportion which, owing to a variety of causes, can never be obtained in practice.

When we act upon alcohol with a proportion of sulphuric acid, sufficient to take away the whole of the water, we obtain little or no ether. Olefiant gas is in this case the principal product, mixed, however, with some sulphurous and carbonic acid gases, which are formed by the too energetic action of the sulphuric acid on the carbon of the alcohol. We can at pleasure then convert alcohol either into ether or olefiant gas; though each of those products is always accompanied by others, resulting from a still farther decomposition of that fluid into its ultimate elements.

*Experiments of Mr. Hennell.*—Though the theory of etherification by sulphuric acid, of which the foregoing is an outline, is now generally received by philosophical chemists, yet some of the intermediate changes, which accompany the formation of ether, remain to be explained. When alcohol and sulphuric acid, in equal weights, are put together, with no other heat than that generated by the mixture, the most abundant product, it is remarked by Mr. Hennell, is sulpho-vinic acid, (see page 335,) into which acid about one half of the sulphuric is converted, by union with the elements of olefiant gas, losing at the same time a great part of its saturating power over bases. By distilling the liquid, ether is generated, and the sulpho-vinic acid disappears; the sulphuric acid being gradually, and towards the close of the process entirely, re-developed in the liquid of the retort. According to the new views of Mr. Hennell, the production of sulpho-vinic acid is an essential step of the process of etherification; while MM. Dumas and Boullay are of opinion that the portions of materials,

that generate ether, are altogether independent of those which form sulpho-vinic acid. With MM. Vogel and Gay Lussac, they imagine that hypo-sulphuric acid is produced by the mutual action of sulphuric acid and alcohol, and that the hypo-sulphuric acid, combining with an oily matter, generated at the same instant, forms sulpho-vinic acid. (Ann. de Ch. et de Ph. Nov. 1827, Jan. 1828.) Mr. Hennell, on the other hand, though he does not go so far as to assert that sulpho-vinic acid is a necessary intermediate stage between alcohol and ether, sees no inconsistency in believing that while one portion of the sulpho-vinic acid is resolved into sulphuric acid and ether, another portion may be formed from the free alcohol and sulphuric acid, to be decomposed in its turn. In confirmation of these views, he remarks that in no manner yet devised, can ether be formed from alcohol, without the presence of sulpho-vinic acid. He has obtained ether, too, when no alcohol was present, by distilling sulpho-vinate of potassa with concentrated sulphuric acid; but, when the addition was made to the sulpho-vinate, before distillation, of half its weight of water, no ether, but only alcohol, was generated. Hence the same sulpho-vinic acid, when concentrated, gives ether, and when diluted, alcohol; the hydro-carbon, which, in oil of wine, neutralizes the whole acid, and in sulpho-vinic acid half of it, being, in the latter body, in such a condition that it will unite with the proportion necessary to form ether, or with the larger proportion necessary to form alcohol, according to circumstances. (Phil. Trans. 1828, p. 365.)

When ether and sulphuric acid are heated together, oil of wine and sulpho-vinic acid are among the products, and since the latter, as has just been stated, is convertible into alcohol, we may thus reconvert ether into alcohol. Ether, then, may be formed from alcohol, and alcohol from ether, at pleasure, by throwing the hydro-carbon of those fluids into that peculiar state, which it assumes when combined with sulphuric acid in sulpho-vinic acid.

In a late memoir on this subject, M. Sèrullas expresses his opinion that the sulpho-vinic acid, to which he gives the name of bi-sulphate of ether, loses by successive portions the ether which it contains. At a later period of the distillation, the excess of sulphuric acid in the bi-sulphate is saturated, he supposes, by hydro-carbon generated at this stage of the process.

A neutral sulphate (oil of wine) is thus formed, of which a portion rises in distillation, while another portion is decomposed, giving origin to all the products, known to be volatilized at this period of the operation. Accordingly, he finds that sulphuric ether, formed at the commencement, contains bi-sulphate of ether, and later in the distillation a greater or less quantity of neutral sulphate. These co-products may be separated from the ether by slow evaporation of the latter fluid, and are always left unvolatilized.

*Phosphoric ether* may be obtained by distilling a mixture of thick tenacious phosphoric acid and alcohol. The first product is a portion of unchanged alcohol. After this a liquid passes over, which has an ethereal smell, and a specific gravity inferior to that of alcohol. It is very volatile; requires for solution eight or ten parts of water; boils at 100; and burns with a white flame, without leaving any trace of acid. (Boullay, Ann. de Ch. lxii. 192.)

#### *Second and third Classes of Ethers.*

The second class of ethers comprehends three species, hydrochloric or muriatic, hydriodic, and hydrobromic ethers.

*Muriatic ether* may be prepared by distilling from a retort a mixture of equal measures of alcohol and of concentrated muriatic acid. It is necessary to keep the receiver cool by surrounding it with ice, which is to be supplied as fast as it melts, and also to give vent to the incondensable vapour that is occasionally formed. To obtain this ether in a gaseous state, it may be received in bottles filled with water of the temperature of 68° to 80° Fahr.

The nature of this ether has been differently stated. Boullay considers it as a compound of muriatic acid and alcohol; but Robiquet and Colin, by decomposing it at a red heat in a porcelain tube, obtained a gas composed of 36.79 muriatic acid, and 63.21 olefiant gas, which they consider as its true constituents. This view is confirmed by the observation of Ampère, that the density of muriatic ether is precisely that of muriatic acid gas + the density of olefiant gas. It should consist, therefore, of equal volumes of these two gases, united without any condensation of elements.

The properties of muriatic ether differ from those of sulphuric ether. It passes, at or below 70°, to the state of a vapour, the

sp. gr. of which is 2.2190 (Thomson), air being 1; in a liquid state its sp. gr. at 40° is to that of water as .870 to 1. It dissolves in an equal volume of water, and the solution has a sweetish taste mixed with that of peppermint. It does not redden vegetable blues, nor precipitate nitrate of silver, nor pronitrate of mercury. It is extremely inflammable, and the odour of muriatic acid is developed by its combustion.

*Chloric ether* may be formed by causing a current of olefiant gas, and another of chlorine, to meet in a glass balloon, shaded from the light, taking care that the first-mentioned gas is somewhat in excess. An oily fluid condenses, which may be purified by first washing it with a little water, and then distilling it from fused muriate of lime. It is limpid and colourless, and its smell and taste are both rather agreeable. Its specific gravity is 1.2201; its boiling point 152° Fahr.; its vapour, at 49° Fahr., supports a column of mercury 24.66 inches high; and the specific gravity of this vapour is 3.4434, air being 1. It burns with a green flame, giving out a smell of muriatic acid, and much soot. It is composed of 100 chlorine + 38.88 olefiant gas; and hence it may be inferred to consist of 1 atom of chlorine and 2 atoms of olefiant gas. (Thomson, Werner. Trans. vol. i.; and Robiquet and Colin, Ann. de Ch. et de Ph. i. and ii.)

*Hydriodic ether* was first prepared by Gay Lussac by the distillation of equal volumes of alcohol and of hydriodic acid, sp. gr. 1.700. This ether does not redden litmus; its sp. gr. at 72° Fahr. is 1.9206; it boils at 148°, but cannot be set on fire by bringing an inflamed body near its surface. By keeping, it acquires in a few days a rose colour, from the disengagement of a little iodine.

*Fluoric ether* has been obtained by distilling, in a leaden retort, a mixture of equal parts of fluuate of lime, sulphuric acid, and alcohol. The product of this distillation was again distilled till one-half had come over, to which potassa was added. This precipitated so much silex, as to gelatinate the whole mass, which, on being again distilled, gave a light ethereal liquid of the specific gravity .720. (Nicholson's Journ. viii. 143.)

*Fluoboric ether*.—When a current of fluoboric gas is passed into alcohol, the latter acquires an ethereal odour, and emits fumes. The liquid rectified first from potassa, and afterwards from chloride of calcium, is analogous to sulphuric ether, burns

like it, and without acid fumes. Its specific gravity is 0.75, when not purified by washing with water. As it does not essentially contain any of the acid employed in forming it, it may be ranked with those produced by sulphuric, phosphoric, and arsenic acids. Its formation appears to be owing to the affinity of fluoboric acid for water. It is not accompanied by the production of sweet oil of wine, as in the case of sulphuric ether.

*The third class of ethers*, those that are formed of alcohol united with an oxacid, includes the nitric, acetic, formic, benzoic, oxalic, citric, tartaric, and gallic. They have been attentively studied by Thenard, and more recently by Dumas and Boullay, who have published an elaborate memoir respecting them. (See Ann. de Ch. et de Ph. Jan. 1828.)

Thenard prepared *nitric ether* as follows: Into a retort, he put equal parts (about 16 oz. of each) of alcohol and nitric acid; and adapted to it in succession, by means of glass tubes, five tall bottles, half filled with a saturated solution of muriate of soda. In the last was a bent tube, opening under a jar, to receive the gaseous products. The bottles were surrounded by a mixture of pounded ice and salt, which was stirred occasionally. To commence the operation, a little fire was applied, but it soon became necessary to extinguish it, and to cool the retort. On the surface of the saline solution, in each of the bottles, was found, after the process was concluded, a yellowish liquid, equal in weight to about half the alcohol employed. That in the first bottle was impure; but the remaining four contained nitric ether free from admixture.

To the details of Thenard's method, Dumas and Boullay find it necessary to add, that the smaller the quantities of materials operated upon, within certain limits, the more manageable is the process, and the more abundant the proportion of the product. With 200 grammes (each about  $15\frac{1}{4}$  English grains) of nitric acid and the same weight of alcohol sp. gr. .820, in a retort of the capacity of three pints, it was not found necessary to cool the retort, provided the fire were withdrawn as soon as mutual action commenced. The process went on quietly, and the whole of the ether condensed in the first bottle containing the saline solution. From 45 to 50 parts of ether, purified by the common process, were obtained.

Nitric ether, has a yellowish colour, a strong ethereal odour, and is specifically lighter than water, but heavier than alcohol,



(.836 at 40° Fahr., Dumas.) It dissolves in the latter fluid, but requires for solution 48 parts of water. It reddens litmus; and though this property may be destroyed by a little lime, yet the ether soon becomes acid again by keeping. It is highly combustible at common temperatures; and, under ordinary pressure, the specific gravity of its vapour is 2.628.

By the action of potassa, Thenard converted this ether into hypo-nitrite of potassa and olefiant gas. Dumas and Boullay analyzed it by peroxide of copper, and found it to consist of

	Grains.	In vols.
Carbon .....	32.69	..... 4
Azote .....	19.00	..... 1
Hydrogen .....	6.85	..... 5
Oxygen .....	41.46	..... 2

or, under another aspect,

4 vol. gaseous carbon	} = 1 vol. nitric ether.
5 vol. hydrogen gas	
$\frac{1}{2}$ vol. oxygen gas	
1 vol. azote	} 1 vol. hypo-nitrous acid
1.5 vol. oxygen	

*Acetic ether* may be formed by distilling, 12 or 15 times in succession, concentrated acetic acid (procured from acetate of copper) with alcohol, and returning the distilled liquor to the charge in the retort. The ether, thus produced, may be freed from a redundance of acid, by rectification with a small quantity of potassa. If washed with water, the product is very small in quantity. It is heavier than most other ethers, its specific gravity being .866. It is volatile; boils at 128° (160° F., Dumas); its vapour has a density of 3.067, and burns with a yellowish white flame. During combustion, acetic acid is developed, though none can be discovered in the ether itself.

This process was verified by Mr. Chenevix. By repeatedly distilling a mixture of ten parts of alcohol with ten parts of acetic acid, he ascertained that no change in the specific gravity of the product took place after the first distillation. Seven-twelfths of the acetic acid were decomposed. Dry carbonate of potassa, added in sufficient quantity to absorb all the water, gave a quantity of ethereal liquor, which weighed 7.4 parts, and had the specific gravity of 8.621. Acetic ether, analyzed by Dumas and Boullay, was found to consist of an atom

of ether precisely analogous to sulphuric ether + an atom of acetic acid. (Ann. de Chim. lxi. 45. See also Thenard on the Action of Vegetable Acids on Alcohol, Mem. d'Arcueil, ii. 5, or 37 Phil. Mag. 216, and Dumas and Boullay, Ann. de Chim. et de Phys. Jan. 1828.)

*Ethers* from *benzoic, malic, oxalic, citric, and tartaric* acids, have also been prepared, but not without the intervention of a mineral acid, which renders their existence as distinct kinds of ether somewhat questionable. In the new view which is taken of this class of ethers by Dumas and Boullay, they are considered indeed as formed of sulphuric ether united with their characteristic acids. The nitric, acetic, and benzoic gave, on analysis, results according best with half a volume of ether + half a volume of acid vapour in each volume; the oxalic, with one volume of each condensed into a single volume.

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#### SECTION IV.

##### *Acetous and Acetic Acids.*

These names were applied, by the framers of the new chemical nomenclature, to denote what were supposed to be two distinct acids, common vinegar purified by distillation being termed the *acetous*, and the highly concentrated acid, formerly called *radical vinegar*, being denominated *acetic*. To account for the superior strength of the latter, it was supposed to contain a larger proportion of oxygen, derived from the metallic oxide, from which acetous acid is generally distilled when converted into acetic. The experiments of Adet were the first that cast any doubt upon this conclusion; and though they appeared to be contradicted by the subsequent ones of Chaptal and Dabit, yet they afterwards received the fullest confirmation from the researches of Darracq. The last-mentioned chemist succeeded in converting common distilled into radical vinegar, under circumstances where no farther oxygenation of the acid could possibly take place, *viz.*, by repeated distillation from fused chloride of calcium. Both terms, however, may be retained for the sake of brevity; the *acetous acid* denoting the weak acid obtained by fermentation; and the *acetic*, the acid in its concentrated state.

Acetous acid may be procured by exposing, in casks partly filled, and open to the atmosphere, at a temperature between

75° and 90° of Fahr., the liquid which has been obtained, by the vinous fermentation, from malt, sugar, or other substances. The liquid soon becomes warm; a number of ropy filaments appear; and after several weeks, it will be found to have acquired an acid taste and smell. Little or no gas is evolved; but on the contrary, an absorption of oxygen takes place. There is an essential difference, therefore, between the circumstances attending the vinous and acetous fermentations. To the latter, the access of air is indispensable; whereas the vinous fermentation requires only free egress for the gases produced; nor is it essential as a previous step to acetification: for many liquids containing sugar, mucilage, or starch, become sour at once, without passing through the former change.

Common vinegar, which, in this country, is chiefly prepared from an infusion of malt, sometimes with the addition of sugar or molasses, and in France from weak wines, may be purified to a certain extent, by submitting it to distillation in a glass retort. The best malt vinegar, unadulterated by sulphuric acid or colouring matter, has a specific gravity of 1.0204. When distilled, the first eighth part is of sp. gr. 0.99712, and contains such a proportion of acid, that a fluid ounce dissolves from 4.5 to 5 grains of precipitated carbonate of lime. The subsequent six eighths are of sp. gr. 1.0023, and a fluid ounce decomposes 8.12 grains of carbonate of lime. A similar quantity, of sp. gr. 1.007, decomposes from 15 to 16 grains of precipitated carbonate of lime, or 13.8 grains of marble. (Phillips on the London Pharm. p. 7.) By distillation, however, vinegar can only be imperfectly purified, and it always acquires a burnt flavour. The distilled liquor contains, too, an extractive matter, which Darracq considers as mucilage, and which causes it to become ropy by keeping; and also, as Mr. Chenevix has shown, a portion of alcohol. The extractive matter, it has been found by the latter chemist, cannot be removed by several repeated distillations. In French vinegar, he discovered a larger proportion both of acid and alcohol, with less of mucilage, than in the vinegar of this country. From four pints of distilled French vinegar, he obtained nearly an ounce-measure of ardent spirit.

Acetous acid is prepared, also, in very considerable quantity, by the distillation of wood. The wood is enclosed in iron cylinders or retorts, which are exposed to a red heat. An immense quantity of inflammable gas is produced; and a liquid, called

formerly *pyroligneous acid*, is condensed, which consists of acetic acid holding in solution a quantity of tar and of essential oil. These impurities it is possible to remove entirely; so that the acid, thus prepared, may be employed for all the purposes of vinegar.

A process, for the decoloration of pyroligneous acid and all kinds of vinegar, has been proposed by Figuer. The agent he employs is animal charcoal, which may be prepared by calcining the most compact beef or mutton bones in a crucible, to which a cover must be luted, having a small aperture, to allow the escape of the gases, and of the other volatile substances. Towards the close of the calcination, when no more flame issues, this aperture must be closed, and the heat raised for half an hour. To a wine quart of cold vinegar, an ounce and a half of this charcoal, finely powdered, is to be added, and occasionally stirred. In 24 hours, the vinegar begins to lose its colour, and, in three or four days, is entirely deprived of it. It is then to be filtered through paper, and it will be found (if the charcoal has been well prepared) to retain its acidity, without having acquired any unpleasant flavour. By reducing the quantity of charcoal to one-half, the change is still effected, but more slowly. Animal charcoal has been found, also, by Berzelius to destroy the minute portion of empyreumatic oil which impairs the flavour of even carefully rectified acetic acid. He prefers the charcoal which is produced in the manufactories of prussian blue. It is only necessary to digest the acid with it, and to filter the liquid.

For purposes of experimental research, acetic acid may be prepared by distilling from a glass retort any quantity of the acetate of potassa (which may be obtained under that name at the druggist's) with half its weight of concentrated sulphuric acid. The adopter and receiver should be kept cool during the distillation. The product, which will be found contaminated with a little sulphurous acid, may be put into a bottle, and shaken at intervals for 24 hours with a small quantity of black oxide of maganese. A second distillation will then afford it pure.

Mr. Phillips has given the following, as a good and economical method of preparing acetic acid: Dissolve 10 ounces of acetate of lead (equivalent to about  $4\frac{1}{2}$  ounces of dry acetate of lime, which may be substituted if more convenient) in two pints of distilled or rain water, and add to the heated solution  $8\frac{1}{2}$  ounces of crystallized sulphate of soda, dissolved in a pint of

boiling water. Mix the two solutions, which will be mutually decomposed. An acetate of soda will be formed, and may be decanted, or drained through cloth, from the precipitated sulphate of lead or lime. Evaporate the solution to dryness, taking care to employ a moderate heat at the last; reduce it to powder; and put it into a retort, with three ounces of sulphuric acid, diluted previously with an ounce of water. By distillation at a gentle heat, about  $5\frac{1}{2}$  ounces of acetic acid will be obtained, containing 42 per cent. of real acetic acid. The contamination of the product with a little sulphurous acid is not easily discovered by the smell, on account of the strong odour of the acetic acid; but it is easily discriminated, on drawing a little of the vapour into the lungs, by its causing a sensation like that produced by breathing the fumes of burning brimstone. In this case, the acid must be redistilled from 1-16th or 1-20th its weight of acetate of lead. By using very dry acetate of soda, and very concentrated sulphuric acid, the product will contain, when rectified, 65 or 66 per cent. of real acetic acid; and it may be further strengthened by allowing it to congeal at a low temperature. The congealed portion, when drained from the fluid, and melted, will be found increased in acidity to upwards of 80 per cent.

The sulphate of soda may be washed out of the retort with a little warm water, and used again for decomposing a similar quantity of acetate of lead or acetate of lime; but if the solution contain much uncombined sulphuric acid, it will be advisable to boil it dry, and heat the dry salt sufficiently to expel the redundant acid, before applying it to effect a fresh decomposition. (Ann. of Phil. N. S. ii. 23.)

Lastly, the crystallized bin-acetate of copper (distilled verdgris), contained in a glass retort, which may be nearly filled with the salt, may be submitted to distillation *per se* in a sand-heat. The acid that comes over has a green colour, and requires to be rectified by a second distillation. Its specific gravity then varies from 1.056 to 1.080. If the product be reserved in separate portions, it has been observed by MM. Derosne, that those which are obtained towards the close, though specifically lighter than the earlier ones, are still more powerfully acid, assuming, as the test of their strength, the quantity of alkali which they are capable of saturating. The last products, it was found also, when submitted to distillation, yield a liquid which has even less specific gravity than water.

(Annales de Chimie, lxiii. 267.) This liquid may be obtained, in a still more perfect state, by saturating the latter portions of acetic acid with caustic and solid potassa; the acetate of potassa precipitates; and a fluid swims above it, which may be rectified by distillation at a gentle heat. It is perfectly limpid; has a penetrating taste; is lighter than alcohol; evaporates rapidly with the production of cold when poured upon the hand; and is highly inflammable. It does not redden litmus. Excepting that it is miscible, in any proportion, with water, it has all the qualities of ether, and like that fluid has the power of decomposing the nitro-muriate of gold. MM. Derosne have proposed for it the name of *pyro-acetic ether*. Its production, they observe, is confined to the latter stages in the distillation of acetate of copper, and is owing, they suppose, not to any modification of alcohol, but to changes in the arrangement of the elements of the salt.

These observations are confirmed by the subsequent ones of M. Mollerat. (Annales de Chimie, lxviii. 88.) Examining two portions of acetic acid, which had precisely the same sp. gr. (*viz.*, 1.063), he found that the one contained 87 per cent. of real acid, and the other only 41. The first he is disposed to consider as the strongest acetic acid that can be procured. It may be distilled at a very moderate heat with great rapidity, and without entering into ebullition. To this acid, having the sp. gr. 1.063 (and of which 100 grains required for saturation 250 of sub-carbonate of soda), he gradually added water, and found, though water is lighter than the acid, yet that the density of the mixture increased till it became 1.079. From this point, the additions of water occasioned a regular diminution of specific gravity. M. Chenevix has since observed the same anomaly, in the acid produced from acetate of silver; and Dr. Thomson has given a table (First Princ. ii. 135) from which it appears that the specific gravity of the acid is at a maximum (*viz.*, 1.07132), when composed of 1 atom of acid and 4 atoms of water, or of

Real acid . . . . .	58.1395
Water . . . . .	41.8605
	100.

Acetic acid, thus prepared, has several remarkable properties. Its smell is exceedingly pungent, and it raises a blister when

applied to the skin for a moderate length of time. When heated in a silver spoon over a lamp, its vapour may be set on fire. At the temperature of about  $38^{\circ}$  Fahr. it becomes solid and shoots into beautiful crystals, which again liquefy at  $40^{\circ}$ . Acid of sp. gr. 1.063 crystallizes even at the temperature of  $55^{\circ}$  Fahr. and does not melt again till raised to nearly  $70^{\circ}$ . These crystals, by saturation with alkalis, appear to contain 83 per cent. real acid, (Quart. Journ. vi. 26.) which approaches nearly to an atom of each; for such a compound would require that the acid should contain 84.5 per cent. of real acetic acid. Acetic acid appears not to be easily destructible by heat; for Mr. Chenevix transmitted it five times through a red-hot porcelain tube, with the effect of only a partial decomposition.

*Acetometer.*—It has already been observed that the strength of acetic acid is not accurately represented by its specific gravity, and it had long been desirable to find a test which should express its degree of acidity with uniform correctness. This, it is evident, may be done by determining the quantity of alkaline or earthy substances required for its saturation; for the stronger the acid, the greater the quantity of any alkali or earth, which it will be capable of neutralizing. One hundred parts by weight of real acetic acid are found to neutralize 290 of crystallized, = 107.7 parts of anhydrous, carbonate (or sub-carbonate) of soda. (Vol. i. p. 586.) It is easy then, after ascertaining the quantity of carbonate of soda which any specimen of acetic acid is capable of neutralizing, to calculate its strength by the rule of proportion; or if any other alkaline or earthy compound be preferred as a test to carbonate of soda, the scale of equivalents will at once show how much should be employed of the test which may be substituted.

In the acetometer invented by Messrs. J. and P. Taylor, which has been adopted by the Excise, for determining the rate of duty on vinegar, hydrate of lime is employed to saturate the acid, and the specific gravity of the resulting solution of acetate of lime is made the measure of the strength of the acid. Vinegar containing 5 parts of real acid in 100 parts by weight, or saturating 14.5 of crystals of carbonate of soda (the kind called by the London vinegar makers No. 24), is taken as a standard; and, when neutralized by hydrate of lime, an hydrometer stands in it at the mark on the stem which is called *proof*. To keep the stem of the instrument at the same mark, when immersed

in stronger acids saturated with lime, it is loaded with a series of weights, each of which indicates 5 per cent. of acid above proof, up to 35, which of course contains  $5 + 35 = 40$  per cent. of real acetic acid. (Quart. Journ. vi. 255.) This is the greatest strength at which the duty is levied by the gallon, that on stronger acids being regulated in a different manner.

Gay Lussac and Thenard, and Berzelius, have analyzed acetic acid; the two first by the combustion of acetate of baryta, of known composition, with chlorate of potassa; and Berzelius by the combustion of the same salt, very carefully dried, with peroxide of copper. (Ann. of Phil. iv. 323.) Their results are as follow. One hundred grains of acetic acid consist of

	Carbon.	Oxygen.	Hydrogen.
According to Gay Lussac ..	50.224	44.147	5.629
———— Berzelius ....	46.8	46.9	6.3

The proportions obtained by Gay Lussac and Thenard may be stated also as follows:

Carbon .....	50.224
Oxygen and hydrogen in the same } proportions as in water .....	46.911
Excess of oxygen .....	2.865
	100.

The most probable constitution of acetic acid, derived from the analysis of its salts, is the following:

Carbon .....	4 atoms	....	24	.....	48
Oxygen .....	3 do.	....	24	.....	48
Hydrogen ....	2 do.	....	2	.....	4
			50		100

On the other hand, Dr. Prout having repeatedly performed the combustion of very fine acetate of copper in oxygen gas, satisfied himself that the volume of the gas underwent a change, and hence that the oxygen and hydrogen in acetic acid are precisely in the proportion to form water. (Phil. Trans. 1827.) The equivalent of acetic acid, heretofore denoted by 50, if we adopt his results, must therefore undergo a little change, *viz.*,

Carbon .....	47.05 = 4 atoms	....	24
Water .....	52.95 = 3 atoms	....	27
			100.
	At. weight		51.

Acetic acid forms with the different bases, a class of salts called acetates.



*Acetate of potassa* may be prepared by saturating pure acetic acid with potassa. As found in the shops, it is not crystallized, but occurs in a foliated form, which it has assumed after cooling from a state of fusion. It is very deliquescent, and extremely soluble in water, and soluble in twice its weight of boiling alcohol. It is probably constituted of

Potassa . . . . .	1 atom . . . . .	48 . . . . .	49
Acetic acid ..	1 atom . . . . .	50 . . . . .	51
		98	100

In the crystallized salt, obtained by exposing its solution under an exhausted receiver along with sulphuric acid, Dr. Thomson found two atoms of water to each atom of the dry salt. In a similar manner, he obtained crystals of binacetate containing 1 atom of potassa, 2 atoms of acetic acid, and 6 atoms of water.

*Acetate of soda* may be formed by the direct combination of acetic acid with carbonate of soda; or, it may be prepared by mixing solutions of 1 part acetate of lime, and 2 of crystallized sulphate of soda, = 0.9 desiccated; decanting the liquid part; washing the precipitate with more water; and evaporating the washings to a proper consistency for crystallization. To obtain good crystals, a slight excess of alkali is necessary. These crystals are permanent when exposed to air, require for solution between twice and three times their weight of water at 60°, and are soluble to a considerable extent in boiling alcohol. This salt may be heated to about 550°, with the loss only of its water of crystallization; but at a higher temperature its acid ingredient is decomposed. (Thomson, Ann. of Phil. N. S. ii. 143.) It consists, according to Berzelius, of

	Crystals.	Dry.
Acetic acid . . . . .	36.95 . . . . .	61.689
Soda . . . . .	22.94 . . . . .	38.311
Water . . . . .	40.11	
	100.	100.

Its theoretical constitution is

Acid . . . . .	1 atom . . . . .	50 . . . . .	60.98
Soda . . . . .	1 atom . . . . .	32 . . . . .	39.02
		82	100.

The crystals appear to consist of 1 atom of anhydrous salt = 82 + 6 atoms of water = 54, together 136.

*Acetate of ammonia* derives its chief importance from having been long employed in medicine as a febrifuge, under the name of Mindererus's Spirit. It is difficult to obtain it in crystals; but its solution, exposed *in vacuo* along with strong sulphuric acid, may be made to deposit four-sided oblique prisms which are very deliquescent. It is volatile at 250° Fahr. and condenses in long slender flattened crystals. The recent crystals, according to Dr. Thomson, consist of

Acetic acid	.....	38.46	or 1 atom	= 50
Ammonia	.....	13.08	or 1 atom	= 17
Water	.....	48.46	or 7 atoms	= 63
		100.		130

*Acetate of lime* may, by careful evaporation, be obtained in small silky crystals; in which each atom of the real acetate is united with 6 atoms of water. It is permanent in the air, and very soluble both in water and alcohol. When made as dry as possible, it becomes strongly phosphorescent at about 250° Fahr. It is difficult to render it so dry, as to yield by analysis more than 33.5 or 34 parts of base from 100 of the salt; but Berzelius states its composition to be

Acetic acid	.....	64.218	.....	100.
Lime	.....	35.782	.....	55.74
		100.		

The proportions deducible from the atomic weights of its elements are

Acetic acid	.. 1 atom	....	50	....	64.1
Lime	.....	28	....	35.9	
		78		100.	

An impure acetate of lime, prepared with pyroligneous acid, is very extensively used in the preparation of acetate of alumina for the use of dyers and calico-printers, and of vinegar-makers.

*Acetate of baryta* is a crystallizable salt, (for its form see Ann. of Phil. N. S. vii. 365), which does not grow moist, but rather loses a portion of its water, by exposure to the air. It requires for solution about twelve parts of cold, and not quite two parts of boiling water. Alcohol dissolves only a very small proportion. By distillation *per se*, Mr. Chenevix finds that it gives pure pyro-acetic ether, of the specific gravity 0.845, coloured by a little empyreumatic oil. Gay Lussac and Thénard state its composition to be

Acetic acid .....	43.17
Baryta .....	56.83
	100.

Its atomic constitution, however, should be

Acetic acid	....	1 atom	....	50	....	39.07
Baryta	....	1 atom	....	78	....	60.93
				128		100.

*Acetate of strontia* is more soluble than the last-mentioned acetate, requiring only about twice its weight of cold water for solution. It forms crystals, the shape of which is represented in the *Ann. of Phil. N. S.* vii. 288. Its properties have not been fully investigated. It probably consists of 48.08 acid + 51.92 base.

*Acetate of magnesia* cannot be obtained in crystals, but only in the state of a thick viscid mass, which is extremely deliquescent, and soluble both in water and alcohol.

*Acetate of alumina* is generally formed, by double decomposition, from the mixed solutions of acetate of lead or lime, and sulphate of alumina. It is a compound of considerable importance from its use in dyeing and calico-printing. When applied, however, to these purposes, it contains always a considerable quantity of alum. The properties of the soluble combination of alumina with acetic acid are but imperfectly known, but it seems probable that it is generally a *bin-acetate*. Gay Lussac has found that it has the remarkable quality of being decomposed by heat and of depositing alumina, which it redissolves on cooling. The effect takes place, even in vessels hermetically sealed, and when the solution has an excess of acid, and seems to bear some analogy to the coagulation of animal albumen. (74 *Ann. de Chim.* 93; and 6 *Ann. de Chim. et de Phys.* 201.)

Dr. Thomson formed an *acetate of alumina* by digesting fresh precipitated hydrate of alumina with acetic acid, till the acid was saturated, at the temperature of the atmosphere. When reduced to dryness by a very gentle heat, it formed a white powder, readily soluble in water, of a sweetish taste, and capable of reddening vegetable blues. It consisted of an atom of base, an atom of acid, and an atom of water.

All the *metallic acetates* that are of any importance have

been already described in the history of the individual metals. To our knowledge of the properties general to this class of salts, some valuable additions were made by Mr. Chenevix. (Ann. de Chim. vol. lxxix.) By distilling *per se* the different metallic acetates, that excellent chemist found that the salts with bases of lead, zinc, and manganese, yield a liquid lighter considerably than water, but heavier than alcohol, and containing only a very small proportion of acid. This degree of levity is owing to the presence of a peculiar fluid, which Derosne has termed pyro-acetic ether, but to which, Mr. Chenevix is of opinion, the less definite name of *pyro-acetic spirit* will be better adapted; a name continued to be applied to it by MM. Macaire and Marcet, who have since made it the subject of investigation. (Ann. of Phil. N. S. viii. 69.)

Of all the metallic acetates, tried by Mr. Chenevix, that of silver gave acetic acid of the greatest specific gravity, and of greatest power in neutralizing alkalis. In this respect, it exceeded, by about one-fifth, an equal weight of the acid distilled from copper. It contained, however, none of the pyro-acetic spirit discovered in the acid from copper. The residuum in the retort contained, in every case, a proportion of charcoal. When the acetates of silver, nickel, copper, or lead were distilled, the metal was found in the metallic state; but zinc and manganese were left in the state of oxides.

The *pyro-acetic spirit*, obtained from the acetate of lead, Mr. Chenevix describes as perfectly limpid and colourless. It has a taste, which at first is sharp and burning, but afterwards becomes cool and somewhat resinous. Its smell resembles that of volatile oils, but it is not easy to say of which particular one. Its specific gravity, when rectified by muriate of lime, he states at 0.864; but MM. Macaire and Marcet, at only 0.786. It is very combustible, and burns entirely away with an intense white flame, very different from the blue flame of the *pyroxilic spirit* described in Chap. X. Sect. xii. Its boiling point is 138° Fahrenheit. It is miscible in all proportions with water, alcohol, spirit of turpentine, and all the volatile oils, and, at a temperature considerably below its boiling point, with the fixed oils. When heated, it dissolves sulphur and wax. By decomposition over ignited peroxide of copper, results were obtained, approaching very nearly to 4 atoms of carbon, 2 of oxygen, and 3 of hydrogen. (Macaire and Marcet.)

## CHAPTER XII.

## ANIMAL SUBSTANCES.

THE products of vegetable and of animal life, though they agree in many of their external characters, and even in some of their chemical relations, present several circumstances of distinction, which, in general, sufficiently discriminate the two classes. Animal substances are the results of still more delicate processes, and of a more refined organization; and the balance of affinities, by which they exist, is disturbed by still slighter causes. To the three great components of vegetable matter (oxygen, hydrogen, and carbon) a fourth is, in animal substances, added, and constitutes a large proportion of their structure. To the nitrogen, which they contain, are owing some of the most important qualities that distinguish this class of compounds. Hence it is, that instead of passing through the vinous or acetous fermentations, they are peculiarly prone to undergo putrefaction; and that, during this change, they yield, among other products, both nitrogen gas and ammonia. When exposed to a high temperature, ammonia, cyanogen, and their compounds, are also generated in great abundance; little or no acetic acid is produced; and the coal, which remains, differs from vegetable charcoal, in being much less combustible. This general description, however, though it applies to most individuals of the animal kingdom, is not strictly true with respect to all. Animal jelly, for example, is rendered sour by spontaneous decomposition. A few vegetable substances, it may also be added, gluten for instances, in consequence of containing azote, become at once putrid; and furnish ammonia when decomposed by heat. The same element forms, also, a part of all the vegetable alkalis described in the 17th section of the last chapter.

In the analysis of animal substances, less precision had till lately been attained, than in that of mineral and vegetable products. It may be considered as of two different kinds. By the first we obtain the *proximate* principles of animal matter, or certain compounds, which, we may presume, existed in the animal structure in a state identical with that in which they are

separated, by the simple processes used for their extraction. Thus, by the long continued action of hot water on bones, we form a solution, which separates spontaneously into two distinct substances, fat and gelatine; while the earthy ingredients remain undissolved. The substances, thus obtained, are not very numerous; and to distinguish them from more complicated products, they may be called *proximate animal compounds*. But, by spontaneous decomposition, or by the agency of heat, we give origin to a set of bodies which had no existence in the subject of experiment, the *ultimate elements* of which have been disunited, and recombined in a new manner. Bones, for example, though they contain no volatile alkali, are yet composed, in part, of its elements (nitrogen and hydrogen), which, at a high temperature, unite and generate ammonia.

The method of analysis by peroxide of copper, so successfully applied, by Gay Lussac and Thenard, to the products of the vegetable kingdom, has been extended to animal substances;\* and, in the history of each, the proportion of its ultimate elements will be stated, chiefly on their authority, or on that of subsequent analysts. Animal substances, they observe, contain much more carbon than those derived from the vegetable world; in all of them, the hydrogen is in excess with relation to their oxygen; and lastly, the greater this excess, the more azote they contain. It is remarkable, moreover, that this azote, and the excess of hydrogen, are very nearly in the proportions required to constitute ammonia.

Animal matters, then, such as fibrin, albumen, gelatine, &c., are composed of charcoal; of hydrogen and oxygen, in the proportions required to form water; and of hydrogen and azote, in the proportions necessary to constitute ammonia. They hold, therefore, among animal matters, the same rank that sugar, gum, lignin, &c., possess among vegetable substances. The animal acids, again, consist, probably, of carbon, oxygen, hydrogen, and azote, in such proportions that the oxygen and azote are in excess relatively to the hydrogen. And the animal oils, on the other hand, will in all probability be shown to contain more hydrogen than is sufficient to convert their oxygen

\* Ann. de Chim. xcvi. 53; and Berard, Ann. de Chim. et de Phys. v. 290, where the process is fully described. See also Mr. Porrett's remarks, Phil. Trans. 1815, p. 225; and Dr. Prout's, in the Medico-Chirurg. Trans. viii. 530; and Phil. Trans. 1827.

into water, and their azote into ammonia. Thus animal substances will be divided, like vegetable ones, into three great classes, relatively to the quantities of hydrogen, oxygen, and azote, which they contain.

In addition to the four elementary bodies already mentioned as constituting the main ingredients of animal matter, other elementary substances are found occasionally in small proportion, such as sulphur, phosphorus, iron, and manganese. Some of the salts, as phosphate of lime, occur in large quantity, and others, such as muriates of soda and potassa, &c., are sparingly diffused through a few only of the animal fluids.

The proximate animal compounds are not very numerous; the following list comprehending, perhaps, the whole of those which are sufficiently well characterized, and of general occurrence.

- |              |           |
|--------------|-----------|
| 1. Gelatine. | 6. Resin. |
| 2. Albumen.  | 7. Sugar. |
| 3. Mucus.    | 8. Oil.   |
| 4. Fibrin.   | 9. Acids. |
| 5. Urea.     |           |

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## SECTION I.

### *Animal Jelly, or Gelatine.*

Animal jelly has been generally considered as an ingredient, not only of the fluids of the body, but of the hard and solid parts. Berzelius, however, in his *View of Animal Chemistry*, p. 50, regards gelatine as a *product* of the operation of boiling; and denies its previous existence in any one fluid of the body. But though it must be admitted that gelatine is absent from some fluids, in which it had been supposed to exist, yet it does not seem probable that it is *formed* by the simple process of boiling. The long-continued action of hot water on skin, membranes, ligaments, cartilages, and bones, may be necessary to bring their gelatine into extensive contact with the water, and also to overcome its affinity for the earthy matter with which it is united. On cooling, the solution forms a tremulous and imperfectly cohering mass, well known by the name of *jelly*. If the watery part of this mass be dissipated by a very gentle heat, we obtain a hard semi-transparent substance, which breaks

with a glassy fracture, and, according to the source from which it has been obtained, has the names of isinglass, glue, portable-soup, &c., all of which are varieties of gelatine, with small proportions of other animal compounds, especially albumen. M. D'Arcet prepares gelatine from bones, not by boiling, but by dissolving out the earthy matter by steeping the bones in diluted muriatic acid. The gelatine remains in a solid state, preserving the shape of the bone, and thus furnishing a complete proof that it existed in the bone ready formed. To purify it from small remains of acid and fat, it is plunged for an instant into boiling water, then exposed to a current of cold water, and quickly dried, in which state it is unalterable by keeping. (Phil. Mag. xvii. 17.) Isinglass, however, as the purest form under which gelatine commonly occurs, will be best employed for the exhibition of its chemical properties.

Dry gelatine, when immersed in water, swells considerably, and becomes soft and elastic. At common temperatures, however, it is not dissolved; all that is thus effected being the absorption of a quantity of water, which it loses again by a gentle heat. But in hot water it dissolves very slowly, yet completely, and affords a liquid which again gelatinates on cooling. These alternate solutions and desiccations may be repeated for any number of times, without occasioning any change in the chemical properties of the gelatine which is submitted to them.

The proportion, in which gelatine forms a solution capable of concreting by cooling, has been determined by Dr. Bostock. One part of dry gelatine to 100 parts of water gave a solution that completely stiffened by cooling; but one part of gelatine to 150 parts of water produced a compound, which, though evidently gelatinous, did not assume the concrete form. (Nich. Journ. xi. and xiv.)

Gelatine in a solid state seems to be absolutely indestructible, when kept in a perfectly dry place; but, when in the form of solution or of jelly, it becomes first sour, and afterwards putrid. It affords a most convenient kind of nutriment for conveyance to a distance, and when evaporated at a gentle heat, it is found to retain much of the peculiar flavour of the meat from which it has been prepared.

Gelatine is insoluble in alcohol, but it is not precipitated by that fluid from its watery solution.



It readily dissolves in most of the acids. Isinglass, dissolved by digestion with warm vinegar, forms a very useful and adhesive cement. Nitric acid, even when cold and very dilute, is a powerful solvent of gelatine. When the solution is evaporated, the acid and gelatine react upon each other; nitrous gas is disengaged; and, if the concentration be not carried too far, oxalic and malic acids are obtained from the residuum. Muriatic acid dissolves gelatine, and retains it unchanged in solution. If chlorine gas be passed through a solution of gelatine, white filaments appear, which, when collected, are found to be very flexible and elastic. They consist of gelatine, very little altered, and united with muriatic acid and chlorine. They are insipid; insoluble in water and in alcohol; not putrescible; and, although containing a large proportion of acid, exert a feeble action on blue vegetable colours. Exposed to the air during a few days, at common temperatures, these filaments emit chlorine, and still more abundantly when heated. In alkaline solutions they disappear, and muriatic salts are formed. (Thenard, *Mémoires d'Arcueil*, ii.)

But the most remarkable effect on gelatine is produced by sulphuric acid, by which Braconnot has discovered that it is converted into a substance analogous to sugar. Twelve parts of powdered glue were mixed by stirring with 24 of concentrated sulphuric acid. In 24 hours the liquor had not changed colour; about thrice as much water was added; and the whole boiled for five hours, adding water at intervals to supply the waste. The solution was saturated with chalk, filtered, and left to evaporate spontaneously. In the course of a week, it yielded crystals of a very sweet taste, which, when washed in weak alcohol, pressed in a cloth, redissolved, and recrystallized, were tolerably pure sugar.

This sugar differs from cane sugar in being much more readily crystallized. It is equal in sweetness to grape sugar, and not more soluble in water than sugar of milk. Its solution does not ferment with yeast. When distilled at a red heat, it yields ammonia among other products.

Sugar obtained from gelatine appears to be capable of uniting with nitric acid without decomposition, and of affording a peculiar crystallizable compound. Its formation by sulphuric acid seems to be owing to the abstraction, from the gelatine, of hydrogen and nitrogen in the proportions composing ammonia,

and probably in the absorption of oxygen. (Ann. de Chim. et Phys. xiii.; Quart. Journ. ix. 392.)

Gelatine is soluble in pure liquid alkalis. The solution is a brownish viscid substance, which has none of the characters of soap, and is not precipitated by acids. (Hatchett, Phil. Trans. 1800.) The property of remaining dissolved in alkalis, after adding acids, distinguishes gelatine from albumen, fibrin, and other animal products; and points out a method of separating it from them in analysis. Owing to the solvent power of alkalis, they do not occasion any precipitation in acid solutions of gelatine; but, when added in excess, first saturate the acid, and then dissolve the gelatine.

Several of the metallic salts and oxides have the property of precipitating gelatine; but not so unequivocally as to be good tests of its presence. Goulard's extract of lead (prepared by boiling litharge in distilled vinegar) effects no change in a solution of gelatine. The same may be said of corrosive sublimate (bi-chloride of mercury). Nitrate of silver and nitromuriate of tin produce a slight and almost imperceptible opacity. The addition of nitro-muriate of gold causes a small quantity of a dense precipitate, from a solution containing  $\frac{1}{50}$ th of gelatine, but not from more dilute solutions.

One of the most active precipitants of jelly is tan; and a very convenient form of that test, in which it may be kept without decomposition, Dr. Bostock finds to be the extract of rhatania, digested in hot water, and filtered after it becomes cold. An infusion of 1 ounce of gall-nuts in a pint of water may also be applied to the same purpose. Such is the delicacy of this test, that, when the gelatine composes only  $\frac{1}{5000}$ th part of the solution, a considerable precipitate is produced by the infusion. The stronger the solution of jelly, the more copious is the precipitate; till at length, when the gelatine is in large proportion, a dense coagulum is formed, which, after being dried in the open air, becomes a hard substance with a vitreous fracture. This compound appears to be equally formed when animal solids, composed chiefly of gelatine, are immersed in solutions of tan; as when the skins of animals, for instance, are steeped in an infusion of oak bark. It is perfectly insoluble in water, and incapable of putrefying; and it constitutes the preservative part of tanned leather, to which it imparts the property of resisting the transmission of moisture. The operation of

tanning, then, consists essentially in the attraction of tan from liquors which contain it by the gelatine of the skins.

It would have been an important step towards the accurate analysis of animal substances, if we could have ascertained the quantity of gelatine in any fluid, by precipitating it with tan. But to this there are two obstacles: 1stly, That tan acts, also, on other animal fluids, upon albumen for instance; and 2dly, That into the precipitate of tan and jelly, these substances do not enter in proportions uniformly the same. In general, however, Dr. Bostock has been led to conclude that the compound formed by the union of jelly and tan consists, on an average, of somewhat less than two parts of tan to three of gelatine. And as we always have it in our power to ascertain what quantity of tan is employed in precipitating any solution of jelly, we may, by an easy calculation, approximate the quantity of jelly contained in the fluid we are examining.

Gelatine has been analyzed by Gay Lussac and Thenard, who employed the chlorate of potassa for its decomposition. One hundred parts were found to contain

Carbon .....	47.881
Oxygen .....	27.207
Hydrogen, .....	7.914
Azote .....	16.998

100.

The atomic proportions, most nearly approaching to these results, are

Carbon .....	15 atoms	.....	90	.....	50.00
Oxygen .....	6 do.	.....	48	.....	26.67
Hydrogen ....	14 do.	.....	14	.....	7.78
Azote .....	2 do.	.....	28	.....	15.55
			180		
				100.	

We are not acquainted with those circumstances that occasion the differences in the several kinds of animal gelatine. Some valuable remarks on them may be found in Mr. Hatchett's "Observations on the component Parts of Animal Membrane." (Phil. Trans. 1800.) An account of the methods of making isinglass, glue, &c., may be consulted in Johnson's History of Animal Chemistry, i. 311.

## SECTION II.

*Albumen.*

With the exception of gelatine, no fluid appears to enter so largely into the composition of animal substances as albumen. It forms a large proportion of the blood and of various secretions; and appears to be the chief basis of several of the solids, *viz.*, of the thin membrane which constitutes the cellular texture, as well as of the skin, glands, and vessels that convey the fluids. The white of an egg, though not composed of absolutely pure albumen, contains it sufficiently free from other substances for the exhibition of its properties. These will be found to be the following:

By agitation with water, the two fluids unite, and form a viscid liquid, the component parts of which do not separate by standing. This solution gives a green tinge to some vegetable blue colours; a proof of the presence of uncombined alkali.

At the temperature of 160° Fahr., undiluted albumen becomes solid, or is *coagulated*. When the solid mass is cut into slices, and suffered to remain for some hours, a few drops of a brownish viscid fluid ooze out, amounting to about  $4\frac{1}{2}$  grains from 100 of the albumen originally submitted to experiment. By a long-continued gentle heat, the coagulated substance itself loses at least four-fifths of its weight; and the solid matter is left behind, of a hard brittle transparent form. Hence 100 grains of the white of egg consist of 80 grains of water,  $4\frac{1}{2}$  uncoagulable matter, and only  $15\frac{1}{2}$  of pure albumen. At a temperature considerably below that required for its coagulation, Dr. Bostock finds that it may be dried, and redissolved in water. (Medico-Chir. Trans. ii. 169.) It is of dried albumen, prepared by the careful evaporation of blood, that the powder consists, which is sold in France for the clarification of wines. For this M. Gay Lussac has advantageously substituted one, obtained by the cautious evaporation of whites of eggs to dryness. (Quart. Journ. xv. 385.)

Coagulation by heat is the distinguishing character of albumen, and affords an easy and obvious test of its presence, even when it forms a very minute proportion of certain fluids. By adding it, in gradually diminished quantity, to water, Dr. Bostock found that a solution, containing only  $\frac{1}{1000}$  its weight

of albumen, was rendered perceptibly opaque by a boiling temperature. For all practical purposes, therefore, this may be considered as a sufficiently accurate test of its presence in any fluid.

The uncoagulated part of the white of egg, Dr. Bostock ascertained, was not affected by solution of bi-chloride of mercury, nor by infusion of galls; but was copiously precipitated by subacetate of lead or Goulard's extract. He considers it as a peculiar fluid, to which he has given the name of *mucus*. Dr. Marcet, who finds it to be an ingredient of several morbid fluids, has proposed to call it *muco-extractive matter*. (Med. Chir. Trans. ii. 377.)

Albumen, which has been coagulated by heat, though perfectly insoluble in water, unless by long boiling aided by a Papin's digester, appears to have undergone no change as to its chemical constitution. During coagulation, there is no absorption of oxygen; no gas is extricated; and hence there appears to be no reaction of the principles of the compound on each other. The coagulum is taken up by liquid caustic alkalis with a disengagement of ammonia. From this combination it is precipitated, unchanged, by acids. (Thenard, Ann. de Chim. lxxii. 321.) By long boiling in water, however, though no apparent solution takes place, Mr. Brande obtained, from coagulated albumen, a fluid which had alkaline properties; and which gave, after evaporation, a viscid substance soluble in water. This fluid he apprehends to be a dilute solution of albumen in alkali. (Phil. Trans. 1809.)

Albumen is coagulated by alcohol, and by acids. The coagulum formed by the latter always retains in combination, according to Thenard, a portion of the acid which has been employed. That produced by nitric acid is least soluble; and therefore nitric acid occasions a precipitate from solutions of albumen, though so dilute as not to be affected by other acids. The coagulum produced by acids is redissolved by pure alkalis, even, as Thenard finds, by ammonia, which does not dissolve albumen coagulated by heat. With solutions of the fixed alkalis, albumen forms a saponaceous compound, that admits of being applied to some of the purposes of soap prepared with oils. When digested with concentrated sulphuric acid, coagulated albumen is dissolved, and a dark-coloured solution is formed, similar to that produced by the action of the same acid

on fibrin. But if the heat be applied very cautiously, the liquid assumes a beautiful red colour, not however invariably, the success of the experiment having been found by Dr. Hope, with whom it originated, to depend on slight circumstances. (See Turner's *El. of Chem.*) Similar uncertainty appears, also, to attend the effect of the sulphuric and other acids, not only on albumen, but on other animal fluids. (See Bourdois and Caventou, *Ann. de Ch. et de Ph.* Jan. 1826.)

In the action of phosphoric acid upon albumen, there is something not only remarkable, but obscure; for, though a watery solution of glacial phosphoric acid, of perfect purity, which has been recently ignited, precipitates both animal and vegetable albumen, yet the solution loses its precipitating power if kept a few days. This happens whether kept exposed to, or excluded from, air. The property is again restored by evaporation, ignition, and re-solution of the acid. No satisfactory explanation of this circumstance has occurred to its observers, MM. Berzelius and Engelhart. (*Ann. de Ch. et de Ph.* Sept. 1827.) It belongs, perhaps, to the same class of facts as those noticed by Mr. Clark. (See vol. i. p. 592.)

Alum, probably in consequence of its excess of acid, coagulates albumen, but does not act on very dilute solutions. One part in 500 of water is rendered slightly turbid by a solution of alum; but no precipitate is formed.

The triple prussiate, or ferro-cyanate, of potassa, is an extremely delicate test of the presence of albumen, and may be used to discover it in fluids to which other tests are inapplicable. To enable it, however, to produce a precipitate, a very slight excess of acetic acid should be previously added to the liquid suspected to contain albumen, or else to the test.

Albumen is coagulated by several of the metallic salts. Solution of bi-chloride of mercury, which has no effect on gelatine or mucus, is a delicate test of the presence of albumen. A single drop of the solution, added to a liquor containing  $\frac{1}{1000}$  its weight of albumen, renders it visibly milky; and, at the end of some hours, a flocculent precipitate falls to the bottom of the vessel. The same reagent produces a sensible effect on a liquid, containing only half that quantity, or  $\frac{1}{2000}$  of albumen. Solution of corrosive sublimate, however, does not separate the whole of the albumen, unless heat is employed. The precipitate in that case is a compound of the metallic salt with albumen.

in the proportion of about one of the former to three or four of the latter. From the quantity of the reagent required to decompose completely a solution of albumen, we may infer the quantity of the latter; for three grains of the metallic salt, being entirely decomposed, indicate  $10\frac{1}{2}$  grains of albumen.

Nitro-muriate of tin precipitates albumen, but less actively than the foregoing salt. Water, holding  $\frac{1}{500}$  of albumen, was not altered by this test till after some hours, when it became milky. Nitrate of silver occasions a precipitate; but the effect is equivocal, from its precipitating also the muriate of soda. Nitro-muriate of gold throws down a dense precipitate from a solution containing  $\frac{1}{1000}$  of albumen. Goulard's extract occasions an abundant dense coagulum.

Solutions of albumen are decomposed by the addition of tan. When an infusion of galls, containing  $2\frac{1}{2}$  parts of solid extract in 100, is added to a liquid, of which albumen forms only  $\frac{1}{1000}$  part, no immediate effect is apparent; but, after some time, a precipitate ensues. If infusion of tan be poured into a concentrated solution of albumen, the precipitate has the consistence of pitch; is not susceptible of putrefaction; and, when dry, is brittle like over-tanned leather. The precipitate by tan from diluted albumen, Dr. Bostock observes, is not coherent, subsides very slowly, and can scarcely be separated by a filtre; whereas the precipitate from solution of jelly, of the same strength, is a hard dense substance, which almost immediately separates from the fluid, and may be collected in a distinct mass, the parts of which cohere together.

Albumen, in whatever way it has been coagulated, appears to be slow in undergoing putrefaction. Mr. Hatchett kept it for some weeks under water, without its showing any tendency to pass to that state. According to Scheele, a small portion of coagulated albumen is soluble in diluted acids, and precipitable by the same acids when concentrated. By steeping albumen for a month in diluted nitric acid, Mr. Hatchett converted it into a substance, which was soluble in water, and affected chemical tests like gelatine.

Albumen almost always contains a portion of sulphur in intimate combination, which gives it the property of blackening silver. This effect is often observed to be produced by eggs on spoons of that metal; and blood, evaporated in silver vessels, stains them with sulphuret of silver.

Several theories have been formed of the cause of the coagulation of albumen; but the first probable conjecture on the subject originated with Dr. Thomson. (Syst. of Chem. v. 489.) The fluidity of albumen he supposed to depend on the presence of alkaline matter, and its coagulation on the removal, or on the saturation, of the alkali. This suggestion seemed to be confirmed by some well-devised experiments of Mr. Brande. (Phil. Trans. 1809.) When the white of an egg was exposed to the action of a galvanic battery, a rapid and abundant coagulation took place round the negative pole, while a thin film only collected at the positive wire. This more copious precipitation at the negative pole appears to have been owing to the separation of alkali; and as it required, in order to produce the effect, a comparatively high electrical power, it should appear that the *rapid* abstraction of alkali is necessary to the perfect coagulation of albumen. According to this view, albuminous fluids are compounds of albumen with alkali and water. When heat is applied, the alkali is transferred to the water, and the albumen becomes insoluble. The alkaline liquor, which is thus produced, reacts upon and dissolves a small quantity of coagulated albumen. When alcohol or acids are the coagulating powers, the effect is owing to a like transfer of alkali. It must, however, be acknowledged that the theory is in many respects questionable, and Dr. Bostock has justly remarked that the quantity of free alkali is so minute, as to be scarcely adequate to hold the albumen in solution. (Med.-Chir. Trans. ii. 175.)

When the uncoagulable part of white of egg was exposed to a strong galvanic power, uncombined soda was found in the negative cup; and muriatic acid with a little coagulated albumen in the positive one. Hence fluid albumen contains both free soda and muriate of soda. In the experiments of Mr. Hatchett, 500 grains of dry albumen afforded  $74\frac{1}{2}$  of coal, of which  $11\frac{1}{4}$  were saline matter, composed, beside the salts that have been mentioned, of phosphate of lime, and of phosphate and carbonate of soda.

From the researches of Mr. Brande, it appears that galvanism may be applied to the discovery of very minute quantities of albumen, which are not rendered sensible by any other test. In this way he produced a rapid coagulation, at the negative pole, of several animal fluids, in which albumen had not been supposed to exist. It has been ascertained, also, by Sir E. Home,



that albumen is coagulated by galvanic arrangements of too low a power to affect even the most delicate electrometer; and hence he has proposed albuminous fluids as tests of the presence of small quantities of electricity. (Phil. Trans. 1809.) On the other hand, Lassaigne asserts, that pure albumen is not coagulable by galvanism, and that the effect, when it does take place, is owing to the decomposition of saline matter, the elements of which react upon the albumen. (Ann. de Ch. et de Ph. xx. 97.)

Albumen was found, by Gay Lussac and Thenard, to consist of

Carbon .....	52.883
Oxygen .....	23.872
Hydrogen .....	7.540
Azote .....	15.705
	100.

The nearest approximation of the above proportions to atomic numbers is the following:

Carbon .....	17 atoms	....102	....	53.40
Oxygen .....	6 do.	.... 48	....	25.13
Hydrogen .....	13 do.	.... 13	....	6.80
Nitrogen .....	2 do.	.... 28	....	14.67
		191		100.

It should appear, then, that albumen contains 2 atoms more of carbon, and one less of hydrogen, than are present in gelatine. Dr. Prout, however, who has analyzed albumen with great care, and has made many interesting observations on its formation by the process of animal digestion, (Ann. of Phil. xiii.), found it to be constituted as follows:

Carbon .....	15 atoms	.... 90	....	50.00
Oxygen .....	6 do.	.... 48	....	26.67
Hydrogen ...	14 do.	.... 14	....	7.78
Azote .....	2 do.	.... 28	....	15.55
		180		100.

But this, it may be observed, is precisely the composition of gelatine, deducible from Gay Lussac and Thenard's analysis. Either, therefore, the analytical results must be erroneous in one or both cases, or the difference between albumen and gela-

tine must consist, entirely, in the grouping or arrangement of elements similar as to kind and number.

Besides perfectly-formed albumen, Dr. Prout has noticed a fluid approaching it in some characters, to which he has given the name of *incipient albumen*. It appears to be that substance not completely elaborated, but requiring a further change by the processes of digestion and assimilation. (Ann. of Phil. xv. 25, 274.)

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### SECTION III.

#### *Mucus.*

The term mucus had been employed in a vague and general sense, until Mr. Hatchett, in his valuable paper on the component parts of animal membrane, attempted to assign to it a more definite meaning. (Phil. Trans. 1800.) Jelly and mucus he considers as modifications of the same substance, and as not essentially differing from each other. The latter term he restricts to that animal substance, which is soluble in cold water, and which cannot be brought to assume the gelatinous state. Dr. Bostock, however, has endeavoured to prove that mucus is a distinct fluid, characterized by a train of properties, which are entirely different from those of animal gelatine. (Nicholson's Journal, xi. and xiv.) Fourcroy and Vauquelin have admitted, also, its claim to be considered as a peculiar compound. (Ann. de Chim. lxvii.) They apply the term, in an enlarged sense, to the viscid liquid, which lubricates the mouth, the œsophagus, the stomach, the intestines, and, in general, all the cavities and passages of the body. It differs, they suppose, from vegetable gum in nothing but in containing a proportion of nitrogen. In the description of its characters, however, they are much less precise than either of the English chemists. Berzelius, on the other hand, seems scarcely to admit that any fluid exists which is entitled to the general name of *mucus*; and finds that its chemical characters vary in different parts of the body, according to the purposes which it is intended to fulfil in the animal economy. (View of Animal Chemistry, p. 58.)

The substance, on which Dr. Bostock's experiments were made, was the saliva of the mouth, dissolved in water by agitation. No appearance of coagulation was produced by raising the temperature of this liquid to 212°, nor, when the liquid

was evaporated, and suffered to cool, did it show any tendency to gelatinate.

No distinct effect was produced on the solution of mucus, by adding nitro-muriate of tin, bi-chloride of mercury, or infusions of galls. Sub-acetate of lead (Goulard's extract) occasioned an immediate opacity, and, after some time, a flaky precipitate. Hence the effects, produced by the tanning principle and by Goulard's extract, establish a decided and essential difference between mucus and gelatine. Tan is a most delicate test of gelatine; but does not, in any degree, affect mucus. Goulard, again, is a sensible test of mucus, but not of jelly. Corrosive sublimate, and triple prussiate of potassa, on the contrary, which discover very small proportions of albumen, are not affected by either jelly or mucus.

Dr. Bostock was not able to devise a method of determining exactly the proportion of mucus in any compound fluid. One great obstacle to all attempts of this kind is, that mucus, beside animal matter, appears always to contain saline matter, which acts upon the metallic solutions used as tests; so that it is impossible to say how much of the effect is owing to each of these separate causes. The precipitates, thrown down from mucus by acetate of lead and nitrate of silver, Mr. Brande found to consist both of the muriates and phosphates of those metals. From 1000 grains of saliva, he obtained by evaporation 120 grains of dry residuum, of which 20 grains were saline matter. The proportion of salts, in the mucus of the trachea, was even still greater. This variety of mucus was not coagulated either by heat, by alcohol, or by acids.

In order to obtain mucus free from neutral salts, it occurred to Mr. Brande to attempt their decomposition by electricity. With this view, a mixture of saliva and water was placed in a vessel intermediate between two others, which contained water only (see *i*, fig. 82), and which were connected, the one with the positive, the other with the negative, extremity of a galvanic apparatus. Fibres of cotton connected the central vessel with the two others. In about ten minutes, a considerable quantity of white coagulum was formed upon the cotton on the negative side, but none on the positive. Thus albumen appears to be a constituent part of saliva, though not discoverable by the usual tests. A separation of alkali took place on the negative side; and hence Mr. Brande is disposed to consider mucus as a com-

pound of albumen and muriate of soda, or of albumen and pure soda. The whole of this subject, however, is still obscure; and requires to be illustrated by farther experiments.

When mucus is evaporated to dryness by a gentle heat, no material change is produced in it. The result is a semi-transparent substance resembling gum, and, like it, soluble again in cold water. Neither alcohol nor ether dissolve it. By destructive distillation, it yields only the common products of animal matter. The proportions of its ultimate elements have not yet been made the subject of investigation.

Mucus, as appears from Dr. Marcet's experiments, beside forming an ingredient of several healthy secretions, exists in some morbid fluids, particularly in that effused in all the forms of dropsy.

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#### SECTION IV.

##### *Fibrin, or Animal Gluten.*

Fibrin forms the basis of the muscular or fleshy parts of animals, and is left combined with albumen, when all the soluble parts, consisting of gelatine, osmazome, fat, and various salts, have been washed away by hot water. It may also be obtained from blood, by laying the coagulum on a linen strainer, and pouring water upon it, till a white fibrous matter remains; or by agitating it in a basin, as it flows from a vein, with a bundle of small twigs, which collect it in a stringy form.

For the purpose of submitting fibrin to a series of experiments, Mr. Hatchett obtained it by digesting shreds of lean beef, during 15 days, in water, which was changed daily, the temperature being such as not to excite putrefaction. The shreds of the muscle were then boiled for five hours every day, during three weeks, changing the water at each boiling; and, finally, the residue was put into a press, and dried by the heat of a water-bath.

The following history of the chemical properties of fibrin is derived chiefly from a memoir of Berzelius.

Fibrin is a soft, tenacious, elastic, and consistent solid. It is insoluble in cold water; but water, after being boiled upon it for some hours, is found to have acquired a milky hue, and, on the addition of infusion of tan, affords a precipitate of white and distinct flocculi, which do not cohere like those produced

by gelatine. The liquid, obtained by boiling fibrin, does not gelatinate, to whatever degree it may be concentrated, but gives a white, dry, hard, and friable residue, which is soluble in cold water. By long boiling in water, fibrin loses its property of softening and dissolving in acetic acid.

Alcohol, of the specific gravity .810, converts fibrin into a kind of adipocirous matter, which is soluble in alcohol, and is precipitated by the addition of water. When alcohol, which has been digested on fibrin, is evaporated, a fatty residue is left, which did not pre-exist in the fibrin. By the action of ether, fibrin is converted into a sort of *adipocire*, similar to the preceding, but in much greater abundance, and distinguished by a much more disagreeable odour.

In concentrated acetic acid, fibrin immediately becomes soft, transparent, and, with the assistance of heat, is converted into a tremulous jelly. By the addition of warm water, this jelly is completely dissolved, with the evolution of a small quantity of azotic gas. The solution is colourless, and of a mawkish and slightly acid taste. By sufficient evaporation the gelatinous substance is reproduced, which, when completely desiccated, is a transparent mass, insoluble in water, without the addition of fresh acetic acid. The solution gives a white precipitate with triple prussiate of potassa, and with pure alkali; but a slight excess of alkali redissolves it. Sulphuric, nitric, and muriatic acids also occasion a precipitate, which consists of fibrin and the acid that has been employed. When laid on a filter and washed, a certain quantity of this acid is carried off by the water, and the remaining substance is soluble in pure water.

In weak muriatic acid, fibrin shrinks, and gives out a little azotic gas, but scarcely any portion is dissolved, even by boiling. Concentrated muriatic acid, when boiled on fibrin, decomposes it, and produces a red or violet-coloured solution. Fibrin, that has been digested with weak muriatic acid, is hard and shrivelled. By repeatedly washing with water, it is at length converted into a gelatinous mass, which is perfectly soluble in tepid water. The solution reddens litmus paper, and yields a precipitate with acids, as well as with alkalis.

The action of sulphuric acid on muscular fibre has been attentively examined by Braconnot. A portion of beef in small shreds was steeped in water, washed several times, and pressed to separate every thing soluble. Of this fibre, 30 parts were

mixed with an equal weight of sulphuric acid, which softened and dissolved it, without acquiring colour or evolving sulphurous acid. It was gently heated, and, on cooling, a layer of fat separated from the surface. It was then diluted with water, and boiled nine hours; saturated with chalk, filtered, and evaporated. No sugar was produced, but the extract had a decided taste of osmazome. It was boiled with alcohol, which, on cooling, deposited a peculiar white matter, called by Bracnot *leucine*. In order to purify this new substance, it was dissolved in water, and a little tan added. After some hours the liquor was filtered, and evaporated till a pellicle appeared. Being then left to stand for 24 hours, the bottom of the vessel was covered with small mamillated crystals of a dull white colour, feeling brittle between the teeth, but having an agreeable taste of meat.

Leucine is lighter than water. When heated in a retort, it melts, then sublimes in part, and forms white opaque crystals, and an empyreumatic acid fluid distils over. By the action of nitric acid on leucine, a distinct compound appears to be formed, which affords peculiar salts with the different bases. (Quarterly Journal, ix. 394.)

From fibrin, nitric acid, of the specific gravity 1.25, disengages at first azotic gas, pure and unmixed with nitrous gas. By continuing the digestion 24 hours, the fibrin is converted into a pulverulent mass, of a pale citron colour, which, when placed on a filter and washed with a large quantity of water, becomes of a deep orange colour. This yellow substance was discovered by Fourcroy and Vauquelin, who obtained it by treating muscular flesh with nitric acid, and who gave it the name of *yellow acid*. Berzelius has ascertained that it is a combination of nitric and malic acids with fibrin, which is in some degree altered by the process.

In caustic fixed alkali, fibrin increases in bulk, and, at length, is completely dissolved. The solution is yellow with a shade of green; and is decomposed by acids; but the precipitated fibrin seems to have undergone some change, for it is not, as before, soluble in acetic acid. The compound of fibrin and alkali has not any analogy with soap, which Fourcroy asserts that it resembles.

Fibrin has been analyzed by Gay Lussac and Thenard, and found to consist of

Carbon .....	53.360
Oxygen .....	19.685
Hydrogen .....	7.021
Azote .....	19.934

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100.

According to these results, its atomic constitution is

Carbon .....	18 atoms	.....	108
Oxygen .....	5 do.	.....	40
Hydrogen ....	14 do.	.....	14
Azote .....	3 do.	.....	42

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204

It appears to contain, then, an atom more of carbon, hydrogen, and azote, and an atom less of oxygen, than are found in albumen. But the constitution of fibrin must still be considered as not reducible to strict atomic proportions.

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## SECTION V.

### *Urea.*

Urea may be obtained by the following process: Evaporate by a very gentle heat, a portion of human urine, voided six or eight hours after a meal, to the consistence of a thick syrup. In this state it concretes, on cooling, into a crystalline mass. Pour on this four times its weight of alcohol, and apply a gentle heat, which will effect the solution of the greater portion. Decant the alcoholic solution, and distil it by a water-bath, till it acquires the consistence of syrup, which is to be poured out of the retort. On cooling, it forms a crystallized substance, which is the urea, not however in a state of complete purity.

Urea thus obtained, has the form of crystalline plates, crossing each other in various directions. It has a yellowish white colour; a smell somewhat like that of garlic; is viscid, and difficult to cut; and has an acrid strong taste. It deliquesces, when exposed to the air, into a thick brown liquid. It is extremely soluble in water, and absorbs caloric during solution. Alcohol dissolves it readily, but in less proportion than water; and the alcoholic solution yields crystals more readily than the watery one. Berzelius, by processes which he has not described, obtained urea quite free from colour, and forming distinct prismatic

crystals like nitre. (View of Animal Chemistry, 8vo. p. 101.) Even in this state, he observes, it is still obstinately combined with lactic (impure acetic) acid, lactate of ammonia, and the peculiar animal matter, which always accompanies the lactates. It is this animal matter, which gives the urine its colour.

Dr. Prout was induced by the observation of Berzelius to attempt the preparation of pure urea, and succeeded by the following process: Fresh urine was carefully evaporated to the consistence of syrup, and to this, when quite cold, pure concentrated nitric acid was added by degrees, till the whole became a dark-coloured crystallized mass, which was slightly washed with cold water and suffered to drain. To this mass, a pretty strong solution of sub-carbonate of potassa or soda was added, till the whole became neutral. The solution was carefully concentrated by evaporation, and set aside, in order that the nitre might separate by crystallization. The liquor, drained from these crystals, was an impure solution of urea, which was mixed with a sufficient quantity of animal charcoal to form it into a thin paste. To this, after remaining a few hours, water was added to separate the urea, and the colourless solution was evaporated at a very gentle heat to dryness. From the dry mass, boiling alcohol separated the urea, and left the nitre and most of the saline substances behind; and from the alcoholic solution the urea was obtained pure by evaporation and crystallization, the solution in alcohol and crystallization being repeated if the crystals were coloured.

Urea thus purified most frequently assumes the form of a four-sided prism. Its crystals are transparent and colourless, and have a slight pearly lustre. It leaves a sensation of coldness on the tongue like nitre. Its smell is faint and peculiar, but not resinous. It does not effect the colours of litmus or turmeric. On exposure to the air it slightly deliquesces, but does not seem to be decomposed. At a strong heat it melts, and is partly decomposed, and partly sublimes unaltered. The specific gravity of its crystals is about 1.350. They are soluble in an equal weight of water at 60° Fahrenheit, and to any extent in boiling water. Alcohol at 60° Fahrenheit, dissolves about  $\frac{1}{3}$ th of its weight, and at 212° more than its weight.

The concentrated solution of urea in water yields, on the addition of nitric acid, a copious precipitate of bright pearl-coloured crystals, resembling the boracic acid. Oxalic acid produces the same effect; but in neither of these compounds are



the acids neutralized. The nitrate of urea, Dr. Prout finds to consist of

Nitric acid . . . . .	47.37	= 1 atom . . . .	54
Urea . . . . .	52.63	= 2 atoms . . . .	60
	100.		114

In some states of disease, the urine abounds so much in urea, as to afford scales with nitric acid. To detect it, Dr. Prout puts a little of the morbid urine into a watch-glass, and by means of a dropping tube introduces a little strong nitric acid under it. If spontaneous crystallization occur, an excess of urea is indicated, and its amount may be estimated by the time required for its production, which varies from a few minutes to two or three hours.

When heat is applied to solid urea, it melts, swells, and evaporates, with an insufferably fetid smell. By distillation, it yields about two-thirds its weight of carbonate of ammonia; about one-fourth of benzoic acid; besides carbureted hydrogen, and a residuum composed of charcoal with muriates of soda and ammonia.

Solution of urea, in water, acquires a yellowish brown colour from infusion of galls, but is not precipitated, either by that infusion, or by one of tan. By keeping, it putrefies very slowly; but much more rapidly, if a little gelatine be added. Ammonia and acetic acid are the products of its decomposition. If the solution, instead of being left to putrefy, be kept in a boiling temperature, and fresh water be added as the evaporation goes on, the urea is at length wholly decomposed. The condensed vapour is found to contain carbonate of ammonia; acetic acid is formed; and a portion of charcoal remains in the fluid contents of the retort. It has been ascertained, by those who distil the volatile alkali from urine, in manufacturing processes, that an equal quantity of ammonia is obtained, whether the urine has undergone putrefaction or not.

When a mixture of urea, with one-fourth its weight of diluted sulphuric acid is distilled, a quantity of oil appears on the surface, which concretes by cooling; acetic acid passes over into the receiver; and sulphate of ammonia remains in the retort. The repetition of this process converts the whole of a portion of urea into ammonia and acetic acid.

Nitric acid, when heated, acts rapidly on urea; nitrous, azotic, and carbonic acid gases, are disengaged; and prussic acid and

ammonia are generated. The residuum, when dried and ignited, detonates like nitrate of ammonia.

Muriatic acid dissolves urea without alteration. When a stream of chlorine gas is passed through a solution of urea, the gas is rapidly absorbed; and white flakes are formed, which soon assume a brown colour. After the solution is saturated with gas, the effervescence still continues; and carbonic acid and nitrogen gases are evolved. The residuary liquid contains both carbonate and muriate of ammonia.

Urea is soluble in alkaline solutions; and, at the same time, undergoes a partial decomposition. A strong smell of ammonia arises, probably from the action of the potassa on the muriate of ammonia which is contained in urea. When solid potassa, however, is triturated with urea, the disengagement of ammonia is too great to be explained in this way; and can only be accounted for, by supposing the volatile alkali to be formed by the union of its elements. A strong solution of potassa, heated with urea, produces a similar effect, a large quantity of ammonia being generated. The residuum, diluted with water, effervesces violently from the escape of carbonic acid gas; a flocculent precipitate is formed, which has the qualities of a concrete oil; and the liquor, when distilled, gives both acetic and benzoic acids.

Urea has the property of changing the form of the crystals of muriate of soda; a solution of that salt, mixed with one of urea, affording, on evaporation, octahedral crystals. Muriate of ammonia, on the contrary, which usually crystallizes in octahedrons, has the form of its crystals altered, by similar treatment, to that of cubes.

Of all the animal fluids, urea appears most readily to undergo decomposition, both from spontaneous changes in the arrangement of its elements, and from the action of other substances. From a careful examination of the products of its distillation with oxide of copper, Dr. Prout has given the following as the proportions of the elements of purified urea. One hundred parts consist of

Oxygen . . . .	26.66	= 1 atom or $\frac{1}{2}$ volume	. . . .	8
Nitrogen ..	46.66	= 1 do. or 1 do.	. . . .	14
Carbon . . . .	19.99	= 1 do. or 1 do.	. . . .	6
Hydrogen ..	6.66	= 2 do. or 2 do.	. . . .	2
Deficient ..	.03			

*Synthesis of Urea.*

By the action of cyanic acid upon ammonia, Wöhler observed that, beside oxalic acid, there is formed a white crystalline substance, which, when examined, proved to be urea. (Ann. de Ch. et de Ph. March 1828.) It is best obtained by decomposing cyanate of silver by muriate of ammonia; or cyanate of lead by liquid ammonia. It forms colourless transparent crystals which are small four-sided rectangular prisms. Its solution in water gives, on the addition of nitric acid, precisely the same brilliant scaly precipitate as the natural urea, with which it agrees also in its other properties. Wöhler considered urea as a cyanate of ammonia + an atom of water; and it is remarkable that this view of its nature almost exactly agrees with the analysis of Dr. Prout, for theoretically it should consist of

Oxygen .....	26.24
Nitrogen .....	46.78
Carbon .....	20.19
Hydrogen ....	6.59
	99.80

## SECTION VI.

*Animal Resins.*

The properties of animal resins have not been fully investigated; but, so far as they have hitherto been examined, they appear to differ considerably from those of the vegetable kingdom.

The RESIN OF BILE may be obtained by the following process: To 32 parts of recent ox bile, add one of concentrated muriatic acid. When the mixture has stood some hours, strain it, in order to separate a white coagulated substance. Pour the filtered liquor, which has a fine green colour, into a glass vessel, and evaporate by a gentle heat. At a certain point of concentration, a green sediment falls down, which, after being separated from the liquid part, and washed, affords what has been considered as resin. Berzelius, however (as will be more fully stated in the section on bile), denies that it is a true resin.

The resin of bile has a dark brown colour; but, if spread out fine, on a white ground, it exhibits a bright grass-green.

It is intensely bitter. At about  $122^{\circ}$  it melts, and in a high temperature burns rapidly. It is soluble both in cold and hot water, and still more soluble in alcohol, from which it is in part precipitated by water.

With pure alkalis it combines, and forms compounds, which have been compared to soap. From these it is precipitated unchanged by acids. By adding solution of chlorine to bile, the resinous portion has its properties considerably altered; it acquires the colour and consistence of tallow; melts at  $104^{\circ}$ ; and dissolves in alcohol and in hot water.

Beside this resin, there are several animal substances which possess similar qualities. Such are the ear-wax, ambergris, castor, &c.

*Cerumen*, or *ear-wax*, has an orange-yellow colour and a bitter taste. It melts at a gentle heat, and sinks into paper like an oil. It is extremely combustible, and burns away with a white smoke, emitting an ammoniacal odour, and leaving very little charcoal. With water it forms by agitation a sort of emulsion; alcohol dissolves 5-8ths of it, and the remainder has the properties of albumen. The alcoholic solution, when evaporated, leaves a deep orange residuum which is very bitter, and resembles the resin of bile. Ether also dissolves cerumen, but the solution is less highly coloured than that in alcohol.

*Ambergris* is found floating on the sea within the tropics, sometimes in large masses, and its origin is still matter of conjecture. Though hitherto arranged among animal resins, yet it appears to consist, according to Pelletier and Caventou, chiefly of a substance analogous to that found by Chevreul in biliary calculi, and called by him, *cholesterine*. To this matter, as obtained from ambergris, Pelletier and Caventou have given the name of *ambreine*. It may be extracted by digesting ambergris in hot alcohol of sp. gr. 0.827. On cooling, the alcohol deposits the ambreine in very bulky irregular crystals. It softens at  $77^{\circ}$ , melts at  $86^{\circ}$ , and when raised a little above  $212^{\circ}$  flies off in a white smoke. It is not capable of forming soap with alkalis.

Ambreine, by being heated with nitric acid, is converted into a peculiar acid, to which the name of *ambreic acid* has been given. It is yellow while in mass, but when spread thin is almost white. It has a peculiar smell, and reddens vegetable blues. It is not fusible, even when heated to  $212^{\circ}$ . It is very

sparingly soluble in water, but dissolves copiously in alcohol and ether. It unites with potassa, and forms a salt, which gives a yellow precipitate with muriates of lime and baryta, sulphates of copper and silver, muriates of tin and gold, and some other metallic salts. (Ann. of Phil. xvi. 93.)

*Castor* is found in two small bags in the inguinal regions of the beaver. It is of a yellow colour, and, when fresh extracted, nearly fluid, but by exposure to the air it hardens, and acquires a resinous appearance. Its principal ingredient is a resin, which appears to be analogous to the resin of bile. It contains also carbonates of potassa, lime, and ammonia, mucilaginous extractive matter, and a peculiar volatile oil on which its odour seems to depend.

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## SECTION VII.

### *Animal Sugar.*

Sugar enters pretty largely into the composition of milk; and into the urine, when the latter is altered by the disease called *diabetes mellitus*. It may be obtained from milk by the following process: Let whey be evaporated to the consistence of honey, and allowed to cool. It concretes into a solid mass, which is to be dissolved in water, clarified by white of eggs, filtered, and again evaporated to the consistence of syrup. On cooling, a number of brilliant white crystals are deposited, which are the sugar of milk. A full account of the preparation of this substance, as practised for sale in some parts of Switzerland, may be consulted in the 1st vol. of Johnson's History of Animal Chemistry.

*Sugar of milk* has a sweetish taste, and no smell. It requires for solution seven parts of cold or four of boiling water; and is insoluble in alcohol. In these properties it differs from common sugar, and also in its relation to nitric acid, as will be afterwards stated, under the head of saccholactic acid.

When exposed to heat, this species of sugar melts and burns with the same appearances as common sugar, and with a similar smell.

Gay Lussac and Thenard have obtained, by their analysis of sugar of milk, the following results, which correspond, almost exactly, with those of Berzelius.

Carbon .....	38.825
Oxygen .....	53.834
Hydrogen .....	7.341

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100.

Dr. Prout from his recent experiments, deduces 40 carbon + 60 water as the composition of sugar of milk. (Phil. Trans. 1827.)

*Diabetic sugar.*—The urine of diabetic patients yields sugar, on evaporation, which approaches more nearly in its characters to those of vegetable sugar, but is generally said to be incapable of crystallization. By exposing the solution, however, for some time to the air, and removing occasionally the mouldy scum which is formed, I have obtained beautiful white crystals, not inferior to those of vegetable sugar. Chevreul has, also, obtained similar crystals, which, when drained, then pressed, and dissolved in hot alcohol, gave a solution that by slow evaporation afforded perfectly white crystals. (95 Ann. de Chim. 319.) In its properties, he found diabetic sugar to approach most nearly to the sugar obtained from grapes; and Dr. Prout, by analysis, determined its composition to be precisely similar to that of vegetable sugar. (Med. Chir. Trans. viii. 537.)

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## SECTION VIII.

### *Animal Oils, and Fats.*

Animal oils have many properties in common with those derived from the vegetable kingdom, and are, probably, essentially the same; but both have some peculiarities, which will be stated in describing their chemical properties. The distinction between animal oils and fats, depends principally on the fluidity of the former, at common temperatures; but this difference is of no moment, since the oils are solidified, and the fats are rendered fluid, by reducing or raising their temperature within a moderate range of the thermometer. Of animal oils, whale oil and sperm oil are most generally known in this country; and among the principal varieties of fat, are spermaceti, butter, tallow, lard, suet, &c.

I. WHALE OIL, OR TRAIN OIL, is extracted from the *blubber* of the whale (principally the *balæna mysticetus*). Originally

it is a firm solid fat, but on reaching this climate, is found to be mostly resolved into a fluid. To obtain the oil, the blubber is melted in large copper vessels. Besides the oil, a quantity of water separates, and on the surface there floats a solid matter called *fenks*, which is probably coagulated albumen. The more moderate the heat, and the shorter its duration, the paler and better is the oil, but this occasions a smaller quantity to be produced. The deep colour is owing partly to too great heat in the boiling, and partly to blood and other impurities which are unavoidably mixed with it. What is extracted in Greenland is perfectly pale and limpid, and free from smell, and burns with a much purer and brighter flame, than what is made in this country. In the early period of the Greenland fishery, the blubber was converted into oil in those regions; but the site of the fishery is now so much changed, and its extent so much increased, as to render this no longer practicable. (Scoresby's Arctic Regions.)

Whale oil requires to be kept in close vessels, to prevent the action of the air, which seems in time to injure it. It is rendered more fluid and combustible by adding a little cold-drawn linseed oil; but it cannot, by any treatment, be made so fit for burning in lamps as spermaceti oil. Perhaps the best way of using it, will be found to be the converting it into oil gas. It may be deprived, however, of its offensive odour by several processes, described by Mr. Dossie in the 15th vol. of the Phil. Mag.; or by chloride of lime, employed in the manner recommended by Mr. Davidson (Brewster's Edinb. Journ. July 1827).

The specific gravity of whale oil is 0.9191. It boils at  $640^{\circ}$ , and may be distilled; but its properties are then materially altered, or rather it becomes a new substance, its specific gravity being diminished to 0.868, its boiling point lowered, and its inflammability much increased. By long continued heat, without being volatilized, it undergoes a series of changes, which are minutely described in the 54th vol. of the Phil. Mag. and also by Dr. Bostock, in the Ann. of Phil. N. S. i. 47.

Dr. Thomson (Syst. of Chem. iv. 433) analyzed whale oil, and found it to consist of

Carbon	.....	12 atoms	....	72	....	68.87
Oxygen	.....	2 do.	....	16	....	16.10
Hydrogen	.....	17 do.	....	17	....	15.03
				105		100.

II. SPERM OIL, or SPERMACETI OIL, forms part of the oily substance found in the cranium of the *physetor macrocephalus*, or spermaceti whale. The oil is separated by putting the mass into a woollen bag and pressing it, by which the fluid is made to run out, and the solid residue, when washed with a weak alkaline ley, affords spermaceti.

Spermaceti oil is much purer than train oil, and burns away, without leaving any charcoal on the wicks of lamps. It has been decomposed by Dr. Ure, by peroxide of copper, and found to consist of

Carbon	.....	10 atoms	....	60	.....	78.00
Oxygen	.....	1 do.	....	8	.....	10.20
Hydrogen	....	9 do.	....	9	.....	11.80
				77		100.

In addition to the ingredients of vegetable oils, a principle is found in animal oils, especially in that derived from *delphinus phocæna*, or sea-hog, to which Chevreul has given the name of *phocénine*. It may be extracted by agitating hot alcohol with the oil, and allowing the liquid to stand twenty-four hours. The alcohol dissolves a portion which floats at the top; and the solution, being decanted and distilled, leaves in the retort an oily matter, which, being treated with cold and weak alcohol, furnishes phocénine. It is fluid at the temperature of nearly 0 Fahr., has a slight smell, has no reaction on litmus, and is soluble in hot alcohol. Potassa converts it into *phocénic acid*, and this also is the effect of concentrated sulphuric acid. The same acid is formed by saponifying the oil itself with potassa; a *phocénate* of that base being produced, from which the potassa may be detached by tartaric acid.

III. The FAT of animals may be separated from the membranous and other substances, with which it is united, by melting it at a gentle heat, with the addition of a small quantity of water. Fat, which has been thus prepared, is called *lard* when of a soft consistence, and *tallow* when harder.

Animal fat is insipid and sometimes free from smell; at others it has a distinct and peculiar odour. It is apt to become rancid by keeping, owing probably to the oxygenation of some animal substance, which the fat contains.

Fat is insoluble in water, and in alcohol at common tempera-



tures. When fresh and pure, it has no action on vegetable blue colours.

Hydrogen, carbon, and azote, do not act on fat. Iodine, chlorine, sulphur, phosphorus, and the metals affect it, precisely as they do vegetable oils.

Fat melts at a degree of heat, which varies in different species; and hence it appears in all forms between a soft solid and a firm consistent mass. Lard becomes fluid at about  $92^{\circ}$  Fahr., and tallow a few degrees higher. At a low red heat, tallow is decomposed, and yields, among other products, a large quantity of olefiant and other combustible gases, but no azotic gas. Hence its fitness for artificial illumination. When less strongly heated in a retort, it yields, according to Bussy and Lecanu, various condensible products, *viz.*, margaric, oleic, and sebacic acids; an oil which is almost inodorous; an empyreumatic and comparatively fixed oil; and a peculiar matter which is volatile, has a strong odour, is soluble in water, and not acid. After these, an oil passes over, holding acetic acid in solution, sparingly soluble in alcohol, not saponifiable by potassa, and which burns after the manner of essential oils; and finally a small quantity of a reddish yellow solid, having the fracture of bees'-wax, transparent, inodorous, insipid, fusible below  $212^{\circ}$  Fahr., and very soluble in ether. There remains in the retort a spongy coal, difficult to incinerate. The condensible products, obtained by distilling animal oils, resemble those of vegetable oils, and differ chiefly in their proportions. Less margaric acid, for instance, is obtained from the vegetable class.

If fat be melted with about one-sixteenth its weight of nitric acid, the mixture being kept fluid, and constantly stirred for some time, a considerable change is produced in its appearance. Nitric oxide and nitrogen gases are evolved; and the lard becomes granular, of a firmer consistence, and soluble in alcohol. Any adhering acid may be removed by washing it with water. In this state, it has been called by the French chemists *oxygenated fat*.

#### *Stearin, Elain, &c., of Animal Fat.*

It has been shown by the experiments of Chevreul, to whom we owe our first correct knowledge of this subject, (Ann. de Chim. tom. lxxxviii. xciii. xciv. xcv., and Ann. de Chim. et Ph. vol. ii. &c.) that fat is not homogeneous, but composed of two

distinct substances. When hogs-lard is heated with alcohol, sp. gr. .800, the fluid on cooling deposits white crystalline needles, which may be purified by dissolving them in fresh alcohol, and allowing them to crystallize a second or even a third time. To the solid thus obtained, Chevreul has given the name of *stearin* from *στέαρ*, tallow. It is white, brittle, and free from taste and smell, and in appearance resembles wax. Its point of fusion varies from 109° to 120° Fahr. according to the source from which it has been obtained. It is soluble in heated alcohol; and is convertible into an acid, named the *stearic*, by being treated with alkalis. This acid is always generated by the action of alkalis on the fat of mutton, beef, or pork; and from the first kind, after being saponified by potash, and decomposed by tartaric acid, another acid, considered as distinct, and named the *hircic*, has also been obtained.

When the alcoholic solution of fat, after having deposited all its stearin, by keeping it at a cool temperature, is submitted to distillation, there remains an oil, which is fluid at 59° Fahr., and is called by Chevreul *elain* (from *ελαιον*, oil). It has generally both colour and smell, but these are not essential to it, and depend on the source from which it has been obtained. It is convertible into soap with alkalis.

Braconnot separated stearin and elain from each other, by simply pressing fat between folds of blotting-paper, which imbibes only the elain, and again gives it out on being moistened with water and submitted to pressure. The proportion of the two ingredients differs considerably in different varieties of fat. Stearin being the cause of hardness is, of course, most abundant in fat of firmest consistence. M. Pelet employs another process, founded on the property that stearin possesses, of being saponified at common temperatures by strong alkaline lixivia, which does not belong to elain. To separate these two substances, when existing together in any oil, he pours upon the oil a concentrated solution of caustic soda, agitates the mixture, and heats it gently, to detach the elain from the soap of the stearin; he then throws it upon a linen drainer, and finally separates by decantation the elain from the excess of the alkaline solution. The elain thus procured is identical with that obtained by the processes of Chevreul and Braconnot. (Ann. de Ch. et de Ph. xxii. 330.)

When hogs-lard is made into a soap with potassa, and this soap

is put into water, it is partly dissolved, and partly deposited in pearl-coloured scales. These scales consist of potassa united with a peculiar acid, which may be separated by adding a due quantity of muriatic acid, and will then float on the surface of the liquor. Chevreul at first gave it the name of *margarine* (from *μαργαρίτης*, a pearl), but afterwards proposed that of *margaritic acid*, which has since been abbreviated into *margaric acid*. It is tasteless, but reddens litmus, is fusible at  $134^{\circ}$ , and, on cooling, shoots into brilliant white needles; floats on water, and is insoluble in it; but is soluble to great extent in alcohol. It has been found, both free and combined with bases, in putrefied curd of milk. It unites with bases, and constitutes salts called *margarates*. With potassa it combines in two proportions, *viz.*, that of 100 acid to 8.80 potassa, and of 100 acid to 17.77 potassa. It is also capable of uniting with other salifiable bases.

That portion of the soap of hogs-lard, which remains dissolved in water, is a compound of potassa with a different acid, mixed however with some proportion of the margaritic. To separate this acid, the soap was decomposed by tartaric acid; the *oleic acid* thus obtained was again saturated with potassa; and the compound again decomposed by tartaric acid. After two or three repetitions of this process, an oily fluid was obtained, destitute of smell and colour; of the specific gravity .899; and remaining fluid till cooled to  $35^{\circ}$ , or, in some of its varieties, to  $43^{\circ}$ . This acid does not unite with water, but is very soluble in alcohol. It unites, also, with salifiable bases, and forms a variety of salts or soaps, the precise composition of which has been stated by Chevreul. (Ann. de Ch. xciv. 263.)

The margaric, and other acids accompanying it, are not supposed to exist ready formed in fat, but to be the results of new affinities, brought into action by the conjoined operation of heat, and of acid or alkaline substances. *Saponification*, therefore, does not consist in the mere union of animal oils or fat, as such, with alkaline bases; but in the formation of stearic, margaric, phocenic, and a few other acids, and in the combination of those acids with bases, forming true salts. In these salts, the proximate elements exist in atomic proportions; but different soaps contain different salts. The soaps made with the fat of pork, mutton, beef, and a few others, are chiefly composed of stearate, margarate, and oleate. Human fat gives chiefly margarate and oleate; and that of the sea-hog contains

phocenate, margarate, and oleate. Their solubility varies with the base, those of potassa, soda, and ammonia, being soluble; while baryta, strontia, and lime, form insoluble soaps.

A very remarkable experiment has been performed by Berard, the result of which was the production of a substance, resembling fat, from bodies in a gaseous state. It consisted in mixing together 1 vol. of carbonic acid, 10 vols. of carbureted hydrogen, and 20 vols. of hydrogen, and passing the mixture through a red-hot porcelain tube. The result was a solid in small white crystals, lighter than water, soluble in alcohol, and fusible by heat into a fluid resembling a fixed oil. (Thomson's Annals, xii. 41.) Doebereiner is said, also, to have obtained a similar product by igniting a mixture of coal gas and aqueous vapour.

IV. SPERMACETI, called by Chevreul *cetine* (Ann. de Chim. et de Phys. vii. 155) when purified, bears some resemblance to wax, but differs from it in other properties. It forms white brilliant plates, soft to the touch, insipid, and having no re-agency on tests. It is more readily fusible, *viz.*, at  $112^{\circ}$  to  $120^{\circ}$  Fahr. and is less soluble in boiling alcohol, of which it requires 150 times its weight. It is copiously dissolved by boiling ether; and the solution, on cooling, becomes a solid mass. Pure potassa acts on it more remarkably than on wax; and the compound is quite soluble, forming a true soap. A heated solution of ammonia affords a liquid, which is not precipitated by cooling, or by the addition of water; but is decomposed by acids. From the solution by potassa, Chevreul separated, by adding a mineral acid, a substance, to which the term *ethal*, compounded of the first syllables of ether and alcohol, has been applied. It is a white solid, fusible at nearly the same point as spermaceti, and on cooling, crystallizing in plates. It is insoluble in water, but much more soluble than spermaceti, in alcohol at  $150^{\circ}$  Fahr., and is susceptible of union with various bases, with which it forms salts or soaps. (Ann. de Ch. et de Ph. xcv. 17.) In these, it is accompanied by oleic and margaric acids.

When spermaceti is distilled, it yields the usual gaseous products, with a greater proportion of olefiant gas. The condensable substances are a large proportion of unaltered cetine, a colourless oil, oleic, margaric, and acetic acids, water, an odorous matter, a yellow matter, and a yellowish empyreumatic oil. Neither sebacic acid, nor the peculiar volatile oil, obtained by

distilling fats, that are formed by stearin and oleine, arises. (Bussy and Lecanu, *Ann. de Ch. et de Ph.* xxxiv. 57.) Ethal, was found, by the same chemists, not to yield acids by distillation.

V. ADIPOCIRE.—A singular instance of the production of animal oil from the lean or muscular part of animals, occurs in the conversion of muscle into a substance resembling spermaceti, and called by the French chemists ADIPOCIRE. To effect this conversion, it is only necessary to confine the fleshy part of an animal in a box, with several holes in it, under the surface of a running stream. When thus confined, the change takes place spontaneously, in the course of a few months. But it may be accomplished much sooner, by digesting animal muscle in strong nitric acid, and washing off the acid by water, as soon as the change has ensued; and it may be bleached, by exposure to chlorine gas. Chevreul and Gay Lussac (*Id.* iv. 71) consider the fatty matter thus obtained to be separated, and not formed, by the processes which have been described. Their inferences, however, are not admitted by Dr. Thomson, who has given a remarkable instance of the actual conversion of fibrin into adipocire. (*Ann. of Phil.* xii. 41.)

Adipocire has a light yellow colour, the consistence of tallow, and a homogeneous texture. It melts at an inferior temperature to either of the foregoing bodies, *viz.*, at  $92^{\circ}$  Fahrenheit. Cold alcohol has little action, but when heated, dissolves about  $\frac{1}{4}$ th or  $\frac{1}{5}$ th its weight. On cooling, it is deposited nearly white, and the alcohol has acquired a yellow tinge. Boiling ether dissolves nearly one-fourth, which separates, almost white, on cooling. Fixed alkalis act on this substance, as on wax and spermaceti, forming with it a soluble soap. Cold ammonia scarcely attracts it, and in this respect it differs from both the preceding substances. Chevreul considers it not as a distinct fatty principle, but as soap consisting chiefly of margaric acid and ammonia, both of which are generated during the decomposition.

VI. CHOLESTERINE. In the greater number of biliary concretions, and constituting the chief proportion of their weight, Fourcroy discovered a substance to which he gave, but erroneously, the name of adipocire. It may be extracted by boiling the finely-powdered calculus with alcohol, from which it separates in a crystallized form on cooling; and it forms a constituent part of the bile of man and several of the lower animals. It has been found also in parts of the body very remote from the

hepatic system, forming the contents of tumours, and of dropsical cysts. Chevreul has shown that it is essentially different both from cetine and adipocire. It appears in white brilliant plates, which are insipid, inodorous, and without action on turnsole. It is not fusible, except by a heat considerably exceeding that of boiling water, *viz.*, 278° Fahr. When distilled, it was observed by Bussy and Lecanu to evaporate, without furnishing any of those acid products, which result from similar treatment of oleine, stearine, and cetine; agreeing in this respect with ethal. It is soluble in boiling alcohol, sp. gr. .816, which takes up 18 per cent. of its weight. It is not altered by alkalis, with which it does not show any tendency to form soap. Chevreul discovered, that when heated with an equal weight of strong nitric acid, a peculiar acid is formed, which he terms the *chlolesteric*. This acid separates on cooling, in the form of a yellow substance. It is scarcely soluble in water, but dissolves in alcohol, and may be crystallized by evaporation. The salts, which it forms with potassa, soda, and ammonia, are very soluble; with other bases it gives compounds which are difficultly soluble. By a heat above that of boiling water, it is decomposed. (Ann. de Chim. et de Phys. vi. 401.) Chevreul has since ascertained the presence of cholesterine in the bile of nine persons of different ages, one of whom had been killed by a fall when in perfect health. It was accompanied by margaric and oleic acids. (Quart. Journ. xviii. 403.)

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## SECTION IX.

### *Animal Acids.*

Of the acids, that have hitherto been discovered to enter into the composition of animal substances, several have already been described, *viz.*, the phosphoric, sulphuric, muriatic, carbonic, benzoic, acetic, and malic. Besides these, the following are either component parts of animal substances, or are formed by treating them with chemical agents:

I. The *uric acid*, or *lithic acid*, exists in human urine, even in its most healthy state, not always uncombined, but generally united with ammonia. The most abundant source of it is in the excrement of the serpent, called *boa constrictor*, and of other amphibia. (Phil. Trans. 1818, p. 303.) Prof. Pfaff, however, finds that this excrement contains so much ammonia,

that it may more properly be considered as a *suburate* of that base. (Ann. of Phil. N. S. vi. 75.) The substance, occasionally voided along with the urine, and called gravel, consists for the most part of uric acid; and this acid forms, also, one of the most common ingredients of urinary calculi. It may be obtained, by dissolving a calculus of this kind (the external characters of which will be hereafter described), reduced to fine powder, in solution of potassa; decomposing the clear solution by muriatic acid *added in excess*; and washing the precipitate with a large quantity of distilled water. The precipitate may be drained, and dried at  $212^{\circ}$ , a temperature sufficient to deprive it entirely of water.

1. Uric acid, when pure, is destitute of colour, taste, and smell; it dissolves in 1720 parts of cold water, or 1150 parts of boiling water; from which, on cooling, much of the acid precipitates. This was the degree of solubility of a specimen which I tried, but Dr. Prout (on Calculous Diseases, p. 14) states that one part of pure uric acid does not dissolve in less than 10,000 parts of water at  $60^{\circ}$ . It is possible, therefore, that my specimen might contain urate of ammonia, which is a much more soluble substance. The solution reddens vegetable blue colours, and combines readily with pure alkalis, but does not effervesce with the alkaline carbonates. The resulting salts, termed *urates* or *lithates*, I have described at length in the Manchester Society's Memoirs, vol. ii. N. S. Fixed alkaline solutions dissolve a considerable quantity of uric acid, if the alkali be in excess. The saturated compounds, however, of uric acid with alkalis, are not much more soluble in water than the acid itself. The combination of uric acid with soda constitutes the principal part of the concretions, found near the joints of gouty persons. (Wollaston, Phil. Trans. 1797.)

2. Nitric acid, diluted with about an equal weight of water, dissolves the uric acid at a moderate heat, and a solution is obtained, which stains the skin permanently of a pink colour; but the colour is not fully developed till the stained part has been exposed to the sun. If the solution be boiled, carbonic acid and nitrogen gases escape, and prussic acid is formed. On evaporation to dryness, a bright red or carmine-coloured mass remains, of which more will be said in connexion with the purpuric acid. By repeatedly distilling nitric from uric acid, the latter is at length wholly decomposed; carbonic acid and nitrogen gases

are evolved; and a strong smell of prussic acid is produced. The residuary fluid deposits crystals, which Dr. Pearson found to be nitrate of ammonia. Chlorine gas, passed through water in which uric acid is suspended, occasions the formation of muriate of ammonia, and of oxalic and malic acids.

3. When the uric acid is distilled *per se*, about one-fourth its weight of a yellow sublimate arises, which contains no uric acid; but a new and peculiar one combined with ammonia. A few drops of thick oil make their appearance; and carbonate of ammonia, with some prussic acid, water, and carbonic acid are obtained. In the retort there remains about one-sixth of charcoal. By submitting uric acid to destructive distillation along with oxide of copper, Gay Lussac determined that the carbon is to the azote which it contains, in volume, as 2 to 1; as is also the case in cyanogen. (96 Ann. de Chim. 53.) It has been shown also, by Berard, that in uric acid, the hydrogen is to the oxygen in a greater proportion than in water; contrary to what has been established with respect to vegetable acids. (Ann. de Chim. et de Phys. v. 295.) Dr. Prout has, also, analyzed uric acid by the same process as that of Gay Lussac, and finds it to be composed of

Hydrogen . . . .	2.857	= 1 atom or 1 volume
Carbon . . . . .	34.286	= 2 do. or 2 do.
Oxygen . . . . .	22.857	= 1 do. or $\frac{1}{2}$ do.
Azote . . . . .	40.	= 1 do. or 1 do.

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100.

*Pyro-uric acid.*—This acid, the existence of which had been hinted by Scheele, and some of its compounds examined by myself, has been fully investigated by Chevallier and Lassaigne. (Ann. of Phil. xvi. 25.) They dissolved the yellow sublimate (noticed in the last paragraph) in water, and added sub-acetate of lead. A white precipitate was obtained, which, after being washed with water, was decomposed by sulphureted hydrogen gas. The liquid, when filtered and evaporated, yielded small white needles, which were pure pyro-uric acid.

Of this acid, cold water dissolves about one-fourth of its weight, and the solution reddens vegetable blues. It dissolves in boiling alcohol, and separates, as the solution cools, in small white grains. When heated, it melts, and sublimes entirely in white needles. By being passed through a red-hot glass tube,



it is decomposed, and converted into the common products of animal matter. It dissolves in nitric acid, and, by evaporation of the acid, is obtained unaltered, a character sufficiently distinguishing it from uric acid, which, when thus treated, yields purpurate of ammonia.

With lime, pyro-uric acid forms a crystallizable salt, which melts on applying heat, and assumes on cooling the consistence of yellow wax. It is constituted of 91.4 acid + 8.6 base. Potassa, soda, and ammonia, form with it soluble salts, the two first of which are crystallizable. Its compound with baryta is very sparingly soluble. Its alkaline salts precipitate peroxide of iron, yellow; that of copper, bluish white; and the oxides of mercury, silver, and lead, quite white.

When analyzed by combustion with peroxide of copper it afforded

Carbon . . . . .	12 atoms	.. 72	. . . . .	28.29
Oxygen . . . . .	14 do.	.. 112	. . . . .	44.32
Hydrogen . . . . .	25 do.	.. 25	. . . . .	10.
Azote . . . . .	3 do.	.. 42	. . . . .	16.84
			251	99.45

In this analysis the products, it may be observed, fall short of the original acid by 0.55 per cent.

*Purpuric acid.*—When to a solution of pure uric acid in diluted nitric acid, ammonia is added, so as to neutralize the excess of nitric acid, and the solution is slowly evaporated, its colour gradually becomes of a deeper purple, and dark red crystals soon begin to separate in abundance. These may be dissolved in dilute solution of potassa, and heat applied to the solution till the red colour entirely disappears. The alkaline solution is then to be gradually dropped into diluted sulphuric acid, which saturates both the potassa and ammonia, and precipitates a peculiar acid in the form of a very fine powder, of a slightly yellowish or cream colour, exhibiting a pearly lustre when viewed by a magnifier, and destitute both of smell and taste. It is of greater specific gravity than water; though, from its minute state of division, it subsides very slowly. This powder is the purpuric acid; a title assigned to it by Dr. Prout, from its power of saturating alkalis; though it is not capable of reddening litmus.

Purpuric acid is very sparingly soluble in water, 1000 grains of

which do not dissolve 1-10th of a grain, but the water assumes a purple tint, which it retains when cold. It is insoluble in ether, alcohol, dilute mineral acids, and solutions of oxalic, citric, and tartaric acids. Concentrated mineral acids, and strong alkaline solutions, dissolve it readily. Strong nitric acid decomposes it with heat, and a purple compound is obtained by evaporation to dryness, precisely as if uric acid had been dissolved.

Purpuric acid expels carbonic acid from the alkaline carbonates with the assistance of heat, and affords a class of compounds called *purpurates*. The aqueous solutions of these salts have a beautiful deep carmine or rose-red colour, from which property the specific name of the acid has been derived. This colour is perhaps best shown in purpurate of ammonia, which Dr. Prout supposes to constitute the colouring ingredient of the pink sediment, deposited from the urine of persons labouring under fevers.

By the combustion of purpuric acid with peroxide of copper, Dr. Prout determined it to consist of

Carbon	.... 2 atoms	.... 12	.....	27.27
Oxygen	.... 2 do.	.... 16	.....	36.36
Hydrogen	.. 2 do.	.... 2	.....	4.54
Azote	..... 1 do.	.... 14	.....	31.81
			44	100.*

An acid has also been obtained by Brugnatelli, by acting on uric acid with nitric acid, which he has proposed to call *erythric acid* (from *ερυθράινειν*, to redden) and its compound *erythrates*. (Phil. Mag. lii. 30.) This compound differs essentially from the purpuric acid of Dr. Prout. It may be formed by dissolving pure uric acid in a slight excess of nitric acid, evaporating slowly, and putting the solution by, to crystallize in a cool place. These crystals Dr. Prout supposes to be either a compound of super-nitrate and super-purpurate of ammonia, or a simple compound of nitric and purpuric acid. (Ann. of Phil. xiv. 363.) They turn slowly to a purple colour on exposure to the air, or more rapidly if dissolved in water and mixed with a few drops of liquid ammonia.

Vauquelin, on repeating the experiments of Dr. Prout and

\* Phil. Trans. 1818, p. 423.

Brugnatelli, obtained different results. He recognised two distinct acids, formed by the action of nitric acid on uric acid, the one coloured and forming an insoluble compound with oxide of lead, the other white and yielding a soluble salt with that oxide. He was disposed, however, to believe that these acids are identically the same, and are modified by colouring matter adhering to one of them. Lassaigne, also, has made experiments, which lead him to be of opinion that the acid, examined by Dr. Prout, was not pure, and that when pure it does not form purple combinations. He prefers, therefore, with Vauquelin, to call it the oxygenated uric acid. (Ann. de Ch. et de Ph. xxii. 334.)

II. *Rosacic Acid*.—There is a substance well known to physicians, as a deposit from the urine at certain stages of fever, at the close of attacks of gout, and in other diseases, under the name of *lateritious sediment*, which Dr. Prout considers as chiefly composed of purpurate of ammonia, formed probably by the action of nitric acid on uric acid, in the urinary organs or passages. (On Calculous Diseases, p. 16.) According to Proust, however, this sediment contains, mixed with uric acid and phosphate of lime, a peculiar acid, which he terms the *rosacic*, from its resemblance in colour to the rose. This acid, he observes, differs chiefly from the uric in being very soluble in hot water; in having little tendency to crystallize; and in precipitating muriate of gold of a violet colour. The experiments of Proust have been confirmed and extended, first by Vauquelin and afterwards by Vogel. (96 Ann. de Chim. 306.) The latter chemist finds that concentrated sulphuric acid converts rosacic acid first into a deep red powder, and afterwards into a white insoluble substance which has all the properties of uric acid. Nitric acid effects the same change. It appears, therefore, that the rosacic and uric acids differ but little from each other, and that the transition is easily made from the former to the latter.

III. The *amniotic acid* has been discovered by Fourcroy and Vauquelin, in the liquor of the amnios of the cow, from which, by slow evaporation, it separates in white crystals. It has a brilliant appearance; a slight degree of sourness; reddens vegetable blues; is scarcely soluble in cold water, but readily in hot, from which it separates, on cooling, in long crystals. It is also soluble in heated alcohol. It combines readily with

alkalis and forms neutral salts, from which the amniotic acid is precipitated by other acids. It does not decompose alkaline carbonates; nor does it precipitate salts with earthy bases, nor the nitrates of silver, mercury, or lead. By a strong heat, it is decomposed, emits ammonia and prussic acid, and leaves a bulky charcoal.

IV. The (so called) *lactic acid* forms a component part of sour milk; from which the acid may be obtained by gently evaporating it to about one-eighth; filtering to separate the curd; and adding lime-water to the residue. A precipitate of lactate of lime is formed; from which the acid may be separated by oxalic acid. The lactic acid is thus obtained in an impure state, dissolved in water. Evaporate the solution to the consistence of honey; on this pour alcohol, and filter the solution. When the alcohol is separated by distillation, the lactic acid remains.

This acid has a yellow colour, is not susceptible of being crystallized, and attracts the humidity of the air. It combines with alkalis and earths, and forms deliquescent salts. It dissolves iron and zinc, with a production of hydrogen gas. It unites also with the oxides of other metals. In its properties, it bears most resemblance to acetic acid. Fourcroy, indeed, supposed that it is really the acetic acid, holding in solution a quantity of extractive matter and of the salts contained in whey, which disguise its ordinary properties; and, in this view, Berzelius, who, until lately considered it a distinct acid, has at length declared his coincidence. (Ann. of Phil. N. S. xii. 407.)

V. The *saccholactic*, *saclactic*, or *mucic acid* (the last of which names is considered by Berzelius as improper), is formed by pouring on powdered sugar of milk, in a stoppered retort, four times its weight of nitric acid, and distilling off a considerable portion of the liquor. On leaving it to crystallize, oxalic acid is obtained; but if, instead of this, the liquid be suddenly diluted with water, a white sediment forms, which may be separated by decantation and washing, and the oxalic acid remains in solution.

Saclactic acid may, also, be obtained by pouring on one part of gum arabic in a stoppered retort, two parts of nitric acid; applying heat a short time, till a little nitrous and carbonic acid gases have come over, and then allowing the mixture to cool. A white powder gradually separates, from which liquid is to the

be decanted. The powder, after being washed several times with cold water, is saccholactic acid.

This acid is about one-fourth more soluble in hot than in cold water. Of the former it requires 60 parts. The solution is acid, and reddens the colour of litmus. At a boiling heat, it effervesces with alkaline carbonates; and unites readily with alkalis and earths, forming a genus of salts which are called *saccholactates* or *saclactates*. With potassa, it affords a salt soluble in eight times its weight of cold water, and crystallizable on cooling; and with soda a salt equally crystallizable, and requiring only five parts of water for solution.

The saccholactic acid is decomposed, when distilled at a red heat, and yields an acid liquor, which deposits needle-shaped crystals. An empyreumatic oil is also formed, and a considerable quantity of carbonic acid and hydro-carburet gases. A large proportion of charcoal remains in the retort. Gay Lussac and Thenard, and Berzelius, have determined its composition to be

Carbon .....	33.69	.....	33.430
Oxygen .....	62.69	.....	61.465
Hydrogen .....	3.62	.....	5.105
	100.*		100.†

Calculating on the results of Berzelius's experiments, saclactic acid should consist of

Carbon .....	6 atoms	....	36	....	34.28
Oxygen .....	8 do.	....	64	....	60.95
Hydrogen .....	5 do.	....	5	....	4.77
			105		100.

Saclactate of lead has also been analyzed by Berzelius, with a result which confirms the above equivalent number. It was found to consist of 100 saclactic acid + 106.87 protoxide of lead, numbers which have as nearly as possible the proportion of 105 to 112, the equivalent of the protoxide.

VI. *Sebacic acid*.—According to Thenard, the acid which has been described as the sebacic, obtained by adding finely-powdered quicklime to melted fat, and disengaging the acid by the sulphuric, is merely acetic acid, disguised by a little sul-

\* Gay Lussac and Thenard.

† Berzelius.

phurous acid. Besides this, however, a different acid may be procured, by first distilling hogs-lard, and washing the product with hot water. The watery solution, poured into one of acetate of lead, gives a flaky precipitate, which is to be heated, along with dilute sulphuric acid, in a retort. No acid is distilled over; but on the surface of the matter in the retort, there floats a substance resembling fat, which may be separated, and washed with boiling water. The water entirely dissolves it, and it becomes concrete on cooling, after which it is to be washed with abundance of cold water.

The acid thus procured, has a white colour; is without smell; has a slightly acid taste, and reddens infusion of litmus. When heated, it melts like a sort of fat; boiling water saturated with it becomes solid on cooling. Alcohol dissolves it copiously. It precipitates acetates and nitrates of mercury and lead, and nitrate of silver. The alkalis are neutralized by it, and form soluble salts, which do not decompose the solutions of lime, baryta, or strontia. It may be volatilized; but requires a higher temperature than benzoic acid, which, in several particulars, it greatly resembles. Berzelius, indeed, considers it as merely benzoic acid, impregnated with other products of the distillation by which it has been obtained, and it is extremely probable that his opinion is well founded.

VII. The *hydro-cyanic acid* is formed, chiefly during the decomposition of animal substances, at high temperatures: or rather, as Gay Lussac has rendered probable, a *cyanide* of *potassium* is formed, which becomes *hydro-cyanate* of potassa, when acted upon by water and an acid conjointly, in the manner already explained in the section on cyanogen.

VIII. The *zoonic acid* has been shown by Thenard to be merely the acetous, holding some animal matter in solution.

IX. The *formic acid*, or *acid of ants*, was submitted to a course of experiments by Fourcroy and Vauquelin, who inferred that it is merely a mixture of acetic and malic acids. This conclusion was opposed by the experiments of Suersen, who endeavoured to prove that the formic is really a peculiar acid; but its identity with the acetic was again asserted by Fourcroy and Vauquelin, and the only difference between the two acids was alleged to consist in the presence, in the formic, of a little phosphoric acid and animal matter. (Ann. de Chim. lxiv. 48.) Gehlen, however, published a fresh series of experiments, the object of

which was to prove that the formic is really a peculiar acid. Its smell and taste differ, he alleges, entirely from those of acetic acid. When sufficiently cooled, it becomes solid, but does not crystallize. Its specific gravity is 1.1168; when diluted with an equal weight of water, it becomes 1.060; and with twice its weight, 1.0296; in all which respects it differs decidedly from acetic acid, as well as in composing different salts with oxide of copper and other bases. (Thomson's Annals, v. 24.) Doebereiner has formed it artificially, by slightly heating bi-tartrate of potassa or tartaric acid with black oxide of manganese and water. A great quantity of carbonic acid escapes, and a sour colourless liquid distils, which is formic acid. (Ann. of Phil. N S. iv. 310.)

The formic acid is recognised, also, as a peculiar compound by Berzelius. By analysis, he obtained as the ingredients of formic acid,

Carbon .....	32.970
Oxygen .....	64.223
Hydrogen .....	2.807

100.

Reducing these proportions to atoms, we find that formic acid is constituted of

Carbon .....	2 atoms	....	12	....	32.4
Oxygen .....	3 do.	....	24	....	64.8
Hydrogen .....	1 do.	....	1	....	2.8
			37		100.

The equivalent thus deduced differs very little from that derivable from the composition of formate of lead, which Berzelius found to consist of 100 acid + 298.1 base. If these results are worthy of confidence, there is a material difference between the constitution of formic and acetic acids, the latter of which contains 4 atoms of carbon + 3 of oxygen + 2 of hydrogen, and is represented by 50. The acid, to which the formic most nearly approaches, is the oxalic, from which it differs only in containing an atom of hydrogen in addition to the carbon and oxygen.

## CHAPTER XIII.

## OF THE MORE COMPLEX ANIMAL PRODUCTS.

All arrangements of the various substances, that compose the animal body, must, in the present state of our knowledge, be entirely arbitrary; and it can, therefore, be of little consequence which of them is adopted. The most obvious division is that which distributes them into fluids and solids, and this order I shall follow in the description of their individual properties. A minute history, however, of all the variety of animal compounds would be foreign to the purpose of this work, and could not be given without very long details. For this reason, I shall notice, at greatest length, those which are most interesting, from their connexion with animal physiology.

## SECTION I.

*Of the Blood—Respiration, &c.*

The blood, when examined as soon as it has been drawn from the human body, is a smooth and apparently homogeneous fluid; viscid to the touch; and of a specific gravity exceeding that of water, in a proportion which, generally speaking, varies from 1.030 to 1.050. Its temperature is generally from 96° to 98° Fahr. A vapour presently exhales from it, which has a peculiar smell, but which does not, when condensed, afford a liquid differing essentially from water. In a few minutes, a thin film appears on the surface; and, after a short time, the whole mass generally becomes coherent. When it has remained some time in this gelatinous state, a more complete separation of its principles ensues. Drops of a yellowish liquid ooze out from beneath the surface of the mass; and, at length, the whole is resolved into two parts, a firm red substance called the cruor, crassamentum, or clot; and a yellowish liquid termed serum. The proportion of these parts varies considerably; the crassamentum being much more abundant in vigorous, well-fed animals, than in such as have been debilitated by disease or by



poor living. On an average it may amount perhaps to one-third of the whole mass.

The period, at which coagulation begins, varies not only with the condition of the blood itself, but with the circumstances in which it is placed. It commences sooner as the vessel is more shallow; but, on an average, it may be said to begin in about  $3\frac{1}{4}$  minutes, and to be completed in 7. Fourcroy states that, during coagulation, caloric is evolved; and this fact appeared to be established, also, by the experiments of Dr. Gordon, who found the coagulating part of a quantity of blood warmer than the rest, by from  $6^{\circ}$  to  $12^{\circ}$  Fahrenheit. (Thomson's Annals, iv. 139.) Subsequent experiments by Dr. John Davy have however, rendered the fact somewhat questionable, and have led to the suggestion of sources of fallacy in Dr. Gordon's investigation. (Quart. Journ. ii. 246.)

The *serum* is an apparently homogeneous fluid, with a yellowish and sometimes slightly greenish tinge; is unctuous to the touch, and saltish to the taste; and has an alkaline re-agency on blue vegetable colours. Its specific gravity is very variable, but on the average is about 1.025. (Marcet.) When exposed to a heat of  $160^{\circ}$ , and still more readily in that of  $212^{\circ}$ , serum is converted into a pretty firm white mass, resembling the white of a boiled egg; it is, in fact, merely coagulated albumen, the properties of which have been already described. When cut into slices, and subjected to gentle pressure, a small quantity of a slightly opaque liquor, of a saline taste and a peculiar odour, oozes from it, which is called the *serosity*. This fluid has generally been considered as holding gelatine in solution; but Dr. Bostock has found reason to doubt the accuracy of the opinion; in which conclusion he is supported by Brande, Marcet, and Berzelius.

Mr. Brande coagulated two fluid ounces of serum, and digested the coagulum, cut into slices, in four fluid ounces of distilled water, which was afterwards separated by means of a filter. The liquid, when evaporated to half an ounce, gelatinized on cooling, and was precipitated by an infusion of tan; but this effect might equally well have been produced by the presence of albumen; and decisive evidence of the presence of the latter substance was obtained, by placing some of the fluid in the Voltaic circuit, when a rapid coagulation of albumen took place round the negative wire. After having coagulated, by galvanic electricity,

all the albumen of a portion of serum, the residuary liquor gave no indications of gelatine. Mr. Brande, therefore, infers, that the serosity consists of albumen, in combination with a large proportion of alkali. (Phil. Trans. 1812.) Drs. Bostock and Marcet, on the other hand, could discover neither albumen nor gelatine in it, but only a matter distinguished chiefly by negative properties, which the former therefore termed *uncoagulable*, and the latter *muco-extractive matter*.

The serosity, according to Berzelius, contains no sulphuric acid, and only a vestige of the phosphoric; but it consists of water, of pure soda holding albumen in solution, of muriates of soda and potassa, of lactate (impure acetate) of soda, and an animal matter, which always accompanies the lactate, the two last composing, he believes, the muco-extractive matter of Dr. Marcet. The solid contents of the serosity Dr. Bostock finds to vary from  $\frac{1}{40}$ th to  $\frac{1}{70}$ th of its weight; but on an average, they may be stated at  $\frac{1}{50}$ th. It was a subject of controversy, which of the mineral alkalis exists in serum in an uncombined form. Dr. Pearson maintained that it is potassa; but Drs. Bostock, Berzelius, and Marcet have satisfactorily shown that it is soda.

When serum is evaporated, at a heat below that required for its coagulation, it yields a yellowish semi-transparent mass, resembling amber, that splits to pieces in drying, and amounts to about 95 grains from 1000 of serum. This substance softens in water, and becomes gelatinous; and about 36 per cent. of its weight are dissolved, and may be passed through a filter. The insoluble part is albumen; and much of this exists, also, in the filtered liquor, beside the neutral salts, which have already been mentioned.

The mineral acids coagulate serum so completely, that no albumen remains in the serosity. The insoluble compounds, which are produced, exactly resemble those of the same acids with fibrin; and the action of alcohol is the same in both cases. Hence Berzelius contends, that there is very little difference between albumen and fibrin. The only character of distinction between them appears to be, that albumen does not coagulate spontaneously, but requires a high temperature; and from this circumstance, it is less rapidly soluble than fibrin in acetic acid.

The serum of human blood is composed, according to Berzelius, of

Water .....	905.0	
Albumen .....	80.0	
Substances soluble in alcohol, <i>viz.</i> ,		
Muriates of potassa and soda .....	.6	} 10.0
Lactate of soda and animal matter .....	.4	
Substances soluble in water only.		
Soda, phosphate of soda, and a little animal matter	4.1	
Loss .....	0.9	
		<hr/> 1000.

This analysis agrees very remarkably with one of Dr. Marcet, who obtained the following ingredients. The substance, termed by him *muco-extractive matter*, is doubtless lactate (impure acetate) of soda; and the sulphate of potassa, and earthy phosphates, were probably formed by the combustion.

A thousand parts of human serum contain,

Water .....	900.00
Albumen .....	86.80
Muriates of potassa and soda ....	6.60
Muco-extractive matter .....	4.00
Subcarbonate of soda .....	1.65
Sulphate of potassa .....	0.35
Earthy phosphates .....	0.60
	<hr/> 1000.

Vogel considers sulphur as another constituent of serum; for he finds that when serum is kept for some days, at the temperature of between 75° and 90° Fahr. a gas exhales from it, which renders legible characters written on paper with acetate of lead. (Ann. de Ch. vol. 87.) This experiment was found to answer with the bile and urine; but it can scarcely be regarded as a proof, that the blood contains sulphur *as such*, or in any state but that of intimate combination. Vogel has endeavoured to establish the presence of carbonic acid in blood, when recently drawn from a vein (93 Ann. de Ch. 71), and in this he is supported by Mr. Brande; but the fact is differently stated by other chemists. In two instances, Dr. Traill has found a portion of oil, amounting to 4½ per cent, in the serum of morbid blood. (Ann. of Phil. N. S. v. 197.)

The *crassamentum* or clot is resolvable into two parts, *viz.*, what has been called coagulable lymph or *fibrin*, and *red glo-*

*bules*. The separation may be accomplished by long-continued washing with water, which dissolves the red globules only, and leaves the fibrin. Its properties differ scarcely at all from those of fibrin, obtained by the long boiling of muscular flesh.

*Fibrin*, as it is contained in the blood, is held in a state of solution, or rather, according to recent observations of Mr. Bauer, in the state of very minute white globules. It is still a question to what cause its spontaneous coagulation is owing. Sir H. Davy's experiments exclude the influence of gases; for he could not discover any difference in the period of coagulation of venous blood, when exposed to azote, to nitrous gas, nitrous oxide, carbonic acid, carbureted hydrogen, or atmospheric air. (Researches on Nitr. Oxide, p. 380.) *In vacuo*, Mr. Hunter states that it occurs at the usual period: but it is not easy to conceive under what circumstances such an experiment could be fairly made. When intercepted in a living vessel, as by placing ligatures on a vein, Mr. Hewson found that blood remained imperfectly fluid for several hours. That mere rest is not sufficient to produce its coagulation appears, also, from the fact, that the blood continues fluid in cases where the circulation is suspended throughout the whole system; as in fainting, and in suffocation from drowning and other causes. The coagulability of fibrin is destroyed, also, without our being able to explain the fact, in animals killed by electricity and lightning: by a blow on the stomach; by the poison of the viper; by violent passions of the mind; and by adding certain neutral salts to recently-drawn blood. In some diseases, on the contrary, especially in those of an inflammatory kind, its tendency to coagulation is greatly increased; and it appears on the surface of the clot in the form of a tough white or buff-coloured covering, depressed in the centre or *cupped*.

The *red globules of the blood* (that part to which its peculiar colour is owing) were first attentively observed and accurately described by Mr. Hewson. As their name imports, they have a globular figure, which is sufficiently visible with the aid of the microscope. The diameter of these globules is from 1-6000th to 1-4000th of an inch. They appear to dissolve readily in water, and tinge it with their own peculiar colour; but Dr. Young finds that the globule remains entire, though colourless. They are soluble in alkalis, acids, and alcohol, but not in the serum. The watery liquid turns syrup of violets green; and,

after some time, deposits a flocculent precipitate, doubtless from the coagulation of albumen, the presence of which is indicated, also, by the effect of boiling the solution. It seems to consist of albumen, dissolved by an excess of pure soda. When evaporated and calcined in a crucible, a residuum is obtained, amounting to about  $\frac{1}{1000}$  of the weight of solid matter, and composed, according to Fourcroy and Vauquelin, chiefly of sub-phosphate of iron.

It has been contended that the red colour of the blood is owing to the iron which it contains, but this opinion has been opposed by the experiments of Mr. Brande. Berzelius had found that a quantity of oxide of iron exists in the ashes of the colouring matter; while none, or at least an infinitely small portion, is afforded by the other ingredients, of blood. He cut the crassamentum into thin slices, and placed them on blotting-paper; and after this had ceased to draw out any moisture, he dried the slices. Four hundred grains of the dried substance left, after incineration, 5 grains of ashes, which were composed (supposing 100 to have been operated on) of

Oxide of iron . . . . .	50.0
Sub-phosphate of iron . . . . .	7.5
Phosphate of lime with a small quantity of magnesia	6.0
Pure lime . . . . .	20.0
Carbonic acid and loss . . . . .	16.5
	100.

The iron in the colouring matter is not, Berzelius admits, in such a state, as to be capable of being detected by the nicest tests of that metal, until the composition of the colouring matter itself is destroyed by combustion. Nor is there any truth in the synthetic proof alleged by Fourcroy, that *sub-phosphate* of iron dissolves in albumen, and imparts to it a bright red colour, resembling blood.

To procure the colouring matter of blood in a detached state, Mr. Brande employed venous blood, stirred during its coagulation. The fibrin is thus removed; and the colouring matter is diffused through the serum, from which it gradually subsides in a very concentrated form. It retains, indeed, some serum; but this does not interfere with the effects of various agents upon the colouring principle. It is then soluble in water, and in dilute acids and liquid alkaline carbonates. It is not precipitable

by alumina; but when left to stand a few days, in contact with a solution of the crystallized muriate of tin, a bright red powder precipitates, which is a combination of the colouring matter with oxide of tin. This, by keeping in water, sustains no change of colour; but when dried by exposure to air, loses its brilliant tint, and assumes a dull red hue.

The most effectual bases, which Mr. Brande discovered for the colouring matter, are solutions of mercury (especially the nitrate) and corrosive sublimate. When either of those salts was added to a watery solution of the colouring matter, a deep red compound was deposited, and the liquid became colourless. Woollen cloth, also, first impregnated with these solutions, and then dipped into the aqueous solution of colouring matter, acquired a permanent red dye, unalterable by washing with soap. It appeared, therefore, from these experiments, which were confirmed and extended by Vauquelin (*Ann. de Ch. et de Ph. i. 9*), that the colouring principle of the blood is an animal substance of a peculiar nature, susceptible, like the colouring matter from vegetables, of uniting with bases, and admitting, probably, of important use in the art of dyeing. On examining the colouring matter, distinctly from the crassamentum, Mr. Brande did not discover a greater proportion of iron, than in the other principles of blood. (*Phil. Trans. 1812.*)

Berzelius, unconvinced by these statements, still argued that the colouring matter of the blood contains iron, not indeed discoverable by reagents applied to the solution, but decisively proved to exist in its ashes. In every respect, except in containing that metal, the colouring matter of the blood agrees with fibrin and albumen, and he seems disposed to believe that its colour, though not depending on the presence merely of an oxide of iron, may be produced by a compound of which that oxide is an essential part. (*Ann. de Ch. et de Ph. v. 42.*) The subject has since been pursued by Dr. Englehart, in a dissertation, which, in 1825, gained the prize, offered by the medical faculty of Göttingen, for the best essay on the nature of the colouring matter of the blood. He obtained no appreciable portion of iron from albumen or fibrin, if carefully freed from colouring matter, but procured it distinctly from the ashes of the red globules. When chlorine gas was passed through a watery solution of the red globules, the colour disappeared, white flocks fell down, and peroxide of iron was discoverable in the trans-

parent liquid, by all the common tests of its presence. The quantity of iron nearly agreed with Berzelius's estimate. (Jameson's Edin. Journ. Oct. 1826.) Rose also has confirmed the results of Englehart, and has shown that oxide of iron is capable of forming so intimate a combination with albumen and certain other organic matters, that it cannot be precipitated by the usual re-agents. (Ann. de Ch. et de Ph. xxxiv. 268.)

It is probably on the red globules of the blood that the different gases act, which produce such remarkable changes in the colour of the entire fluid. Nitrogen gas blackens arterial blood, and, according to Girtanner, venous blood also. In an experiment of Dr. Priestley, it appeared that the bulk of a quantity of nitrogen gas, to which arterial blood was exposed, sustained a diminution. Blood, which has had its colour thus impaired, it was found by the same philosopher, may be restored to its bright florid hue, by agitation with oxygen gas; and these changes may, at pleasure, be repeated alternately. Oxygen gas, to which blood is exposed, is diminished in volume, and contaminated by carbonic acid. Atmospheric air undergoes the same change in consequence of the oxygen which it contains, but in a less remarkable degree.

Similar alterations are, also, constantly going on in the blood, during its circulation through the living body. In the veins it is of a dark red colour, inclining to purple. In this state it arrives at the right ventricle of the heart, by the contraction of which it is driven into the pulmonary artery. This artery is distributed, by extremely minute ramifications, over the whole surface of the air-cells of the lungs; and, in these, the blood is exposed to the action of atmospherical air, through the slender coats of the blood-vessels. Here it acquires a bright vermilion colour, and, it is said, an increase of  $1^{\circ}$  or  $1.5^{\circ}$  of temperature. Returning to the left ventricle of the heart by the pulmonary veins, it is distributed, by the contraction of this ventricle, through the whole body. In its course it loses its florid colour, and, after traversing the system, returns to the lungs, to be once more fitted for the performance of its functions.

### *Respiration.*

The function of RESPIRATION consists of two distinct actions, that of *inspiration*, by which the air is drawn into the lungs;

and that of *expiration*, by which it was expelled, after having served the purpose for which it was inhaled. By an easy natural inspiration, from 16 to 20 cubic inches may, perhaps, on an average, be the quantity taken in by a man of middle size. By a forced expiration, from 160 to 170 cubic inches may be expelled, after which there still remain in the lungs about 120 cubic inches, making their entire contents about 290 cubic inches. Calculating from the number of inspirations in 24 hours, and the quantity inspired at each, it would appear that about 666 cubic feet of air are breathed during every diurnal period. It appeared, from the experiments of Messrs. Allen and Pepys (Phil. Trans. 1808), that the same quantity is expired, with little if any diminution of volume; but Dr. Edwards has shown that in a great majority of cases, a diminution really takes place, though it is so variable as not to be reduced to any fixed amount. (Bostock's Phys. ii. 101.) After being once only admitted into the lungs, atmospheric air returns charged with 8 or  $8\frac{1}{2}$  per cent. of carbonic acid gas. If the same portion be breathed repeatedly, considerable uneasiness is experienced; but the quantity of carbonic acid cannot be increased beyond 10 per cent. The proportion of that gas, however, which is produced by the same individual, is liable to some variations, which have been described by Dr. Prout (Ann. of Phil. xiii. 269), and by Dr. Edwards. When the state of the expired air is examined by eudiometrical tests, a quantity of oxygen is found to have disappeared, nearly equal in volume to the carbonic acid which has been formed. Now as carbonic acid has been proved to contain exactly its own bulk of oxygen gas, it would appear that the oxygen, absorbed from the air by respiration, must have been expended in forming that acid, entirely, if no diminution of volume is observed; and partly, when the air expired falls short in volume of that inspired. Respecting the carbonic acid, which is found in expired air, it may be doubted whether it is merely *displaced* from the blood by the oxygen absorbed through the coats of the vessels; or, *formed* by the union of the inspired oxygen with the carbon of that fluid. In the latter case, we have the choice of two hypotheses; the one, that the combination takes place, in the lungs, between oxygen and carbonaceous matter exhaled in a vaporous state through the coats of the vessels;—the other, that the combination is effected, as the absorbed oxygen circulates with



the blood throughout the system. The latter view is most consonant with the equable diffusion of heat over the whole body; and with the experiments of Dr. Edwards, which show that carbonic acid exhales from the lungs of frogs confined in hydrogen gas, in a quantity much beyond what can be traced to the air existing in their lungs at the outset of the experiment. Of the two suppositions, the latter, therefore appears to be the most probable.

It was long supposed that the nitrogen of the atmosphere is entirely passive, and that it undergoes neither diminution nor increase by respiration. This was the opinion of Lavoisier, and of Allen and Pepys. Priestley maintained an absorption of nitrogen, but the state of gaseous analysis in his time was too imperfect to establish the fact. On this part of the subject much light has been thrown by the researches of Dr. Edwards, made by confining entire animals in given portions of air. The effect, so far as respects this question, was by no means uniform, there being in some cases an evident increase of nitrogen, in others a deficiency, the latter occurring during winter, and the increase during summer. It appears, then, probable, as Dr. Bostock has observed, that at all times both processes are going forward; that they are often exactly balanced; while in other instances, owing to varied circumstances of age, temperature, &c., either the absorption or exhalation gains an ascendancy, manifested by the composition of the expired air.

Besides carbonic acid, a portion of watery vapour is emitted from the lungs, in a quantity sufficient to be visible when the atmosphere is of a low temperature. From various experiments, it may be inferred to amount to about three grains in a minute. The water thus exhaled may either be generated in the lungs, by the union of the inspired oxygen with the hydrogen of the blood; or it may be nothing more than the condensed vapour of a portion of that fluid, which is ordinarily secreted into the bronchial cells.

An important purpose of the function of respiration is, that it contributes to that equable temperature, which the animal body preserves, amidst all the changes in the surrounding medium. This is peculiarly the property of living matter; for all other bodies have the same degree of heat with the substances that are in contact with them. In the human body, the temperature varies only a very few degrees from  $96^{\circ}$ , whether it be exposed to a cold of many degrees below the freezing point; or

be surrounded by an atmosphere, little short of the heat of boiling water. There must, then, be certain processes in the animal economy, by which, in the former case, caloric is reduced from a latent form to that of temperature; and, in the latter case, by which the great excess of caloric is absorbed, and prevented from becoming injurious by its accumulation.

Notwithstanding the great advances that have been made in our knowledge of the chemical changes effected by respiration, we are still ignorant of those precise differences, which constitute the distinction between venous and arterial blood, or in what way the function of respiration converts the former into the latter. That there is really a chemical difference between them, although perhaps of too refined a kind to be discovered by our imperfect methods of analysis, admits of little doubt, and the constant connexion of arterialization with the conversion of oxygen into carbonic acid, points out the decarbonization of venous blood as the most probable cause of the change. If we were to admit, with Dr. Crawford, a corresponding difference between arterial and venous blood, as to their capacities for heat, this would carry us a step further in explaining the production of animal heat. That ingenious philosopher supposed that he had established by experiment, that the capacity of arterial blood for caloric is superior to that of venous blood, in the proportion of 1030 to 892. When, therefore, arterial blood is converted into venous, a considerable quantity of caloric must pass from a latent to a free state, and must prove an abundant source of temperature. Now this is precisely what is constantly taking place in the body. Caloric is evolved by the combination of the inspired oxygen with carbon; but as the capacity of blood for caloric is, at the same time, enlarged, its temperature is not raised by being thus arterialized. In its progress through the system, the blood again suffers a diminution of capacity; and the caloric, which it had carried in a latent form to the remotest extremities, is extricated, and applied to the support of animal temperature. This theory explains why the heat is not excessive in the lungs, but is equally distributed over the whole body. In animals, placed in a high temperature, Dr. Crawford discovered, that the change of arterial into venous blood does not go on; and no addition of temperature is, therefore, derived from this source. Another cause, limiting the heat of the body under such circumstances, is the excessive evaporation which

takes place from the surface of the skin, and which is indicated by a loss of weight of no inconsiderable amount. (Nicholson's Journal, xvii. 215.) Subsequent experiments, however, by Dr. John Davy, have rendered it doubtful whether any such relation between the specific heats of arterial and venous blood, as that pointed out by Dr. Crawford, really exists; and his observations rather accord with the theory of Black, that animal heat is produced in the lungs, and is distributed over the whole system by means of the arterial blood. Consistently with this explanation, the temperature of the blood in the carotid artery was found to exceed that in the jugular vein from 1.5 to 2 degrees. (Phil. Trans. 1814.) The subject, it is obvious, is still enveloped by great difficulty and obscurity. Of the influence of the nervous system over animal heat, though we know not in what it consists, no doubt can be entertained. It is established by long-known phenomena of disease, as well as by experiments devised for the purpose. (Brodie in Phil. Trans. 1811, 1812.) We are not however, entitled to conclude that the nervous system has, within itself, a power of generating heat; on the contrary, it is more probable that its different conditions influence the activity of vessels and organs, in which processes of a calorific nature are constantly going on.

It is not in the lungs only that the blood exerts an action on atmospherical air; for a similar function, it appears, belongs to the skin throughout the whole body. If the hand be confined in a portion of atmospherical air or oxygen gas, it has been ascertained that the oxygen disappears, and is replaced by a portion of carbonic acid. At the same time, a considerable quantity of watery fluid transpires, and may be collected by a proper apparatus.

The blood is subservient to various important uses in the animal economy. It is a source, from which are constantly prepared a variety of other substances, both solid and fluid, that are essential to our well being, and even to our existence. From the blood is derived the solid matter of the bones themselves; it does not, however, exist in the blood in the state of sub-phosphate of lime or bone earth; but appears to be produced, from the *ultimate* elements of blood, on the very spot where its presence is required. (Berzelius's Animal Chemistry, p. 19.) The muscles, which are affixed to the bones, and which, acting as levers, enable us to change our situation at pleasure, are referrible to the same source; and so also is all the variety of animal

fluids, which perform a necessary part in the economy of this complicated machine. The solids and fluids, thus produced, are sometimes elaborated by complicated organs called glands, and are then termed *secretions*. A sufficiently exact and comprehensive knowledge of the business of secretion would have been attained, if we were able to discover, in the secreted solids or fluids, substances analogous to those which are found in the blood, and no others. But in many secretions we find principles bearing no resemblance to albumen, fibrin, or any of those fluids that form the proximate elements of the blood. In these cases, nature must have gone farther in the work of separation; and, after disuniting the ultimate principles of the blood, have recombined them in a new manner and in different proportions. This is a species of synthesis, which we have hitherto not been able to imitate in substances of the animal kingdom, and in very few instances even in vegetable products.

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## SECTION II.

*Of the Secretions subservient to Digestion; viz., the Saliva, the Gastric and Pancreatic Juices, and the Bile.*

Saliva is a liquid secreted by certain glands, and poured into the mouth, for the purpose of being mixed with the food during mastication. It is a slightly viscid liquor, of a saltish taste, destitute of smell, and of a white colour, or with a slight tinge of blue. Its specific gravity, according to Haller, is 1960 to 1875, or, according to Siebold, as 1080 to 1000. The latter author has compared its consistence to that of a solution of one part of gum in forty parts of water. It is neither acid nor alkaline, and has therefore no effect on blue vegetable colours. Its quantity varies considerably. Nuck has estimated it at eight or ten ounces daily; and, during a mercurial salivation, several pints flow in the same interval. (Fourcroy, *Système*, 4to. v. 268.)

Saliva, when evaporated by a gentle heat to dryness, yields a proportion of dry extract in thin semi-transparent plates, varying from 1 to 25 per cent. If the process be stopped when about a third only remains, crystals of muriate of soda are formed. Exposed to the air, it appears to absorb oxygen, and

becomes of a thicker consistence, whitish flocculi at the same time separating from it.

There is some difficulty in effecting the diffusion of saliva through water; but this may be accomplished by rubbing the two fluids together in a mortar. The solution, which is thus obtained, was subjected to the action of tests by Dr. Bostock. (Nich. Journ. xiv. 147.) Bichloride of mercury produced no immediate effect; but, after some hours, a light flocculent coagulum separated, leaving the liquid nearly transparent. The same test produced a still less striking effect in the filtered portion of some saliva, which had been several days exposed to the atmosphere. Infusion of galls precipitated white flakes from the recent but not from the filtered liquor. The filtered fluid was copiously precipitated by Goulard's extract, and by nitro-muriate of tin. From these experiments, Dr. Bostock infers, that saliva contains coagulated albumen, and also a quantity of mucus and muriate of soda, but no gelatine. Berzelius has published a more specific analysis of saliva. Its constituents are

Water .....	992.9
A peculiar animal matter .....	2.9
Mucus .....	1.4
Alkaline muriates .....	1.7
Lactate of soda and animal matter ..	0.9
Pure soda .....	0.2

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1000.

The latest experiments on saliva are those of Tiedemann and Gmelin. They find three proximate animal principles, *viz.* proper salivary matter, mucus, and osmazome, with sometimes a little albumen, and a minute portion of phosphorus dissolved in fatty matter. The soluble salts are six; an alkaline acetate, carbonate, phosphate, sulphate, muriate, and sulpho-cyanate, the last mentioned of which imparts to saliva those properties, which had been ascribed to uncombined alkali. In man, the base of these salts is potassa, while in the dog and sheep it is mostly soda. Sulpho-cyanic acid is most abundant in human saliva, and is scarcely perceptible in that of the dog. The insoluble salts are phosphate of lime, and carbonate of lime and magnesia in very small quantity. (Bostock's Physiol. iii. 422.)

When exposed to the agency of galvanic electricity, Mr Brande, found that saliva, even after being first boiled in water,

gives an abundant coagulation, and a separation of alkali round the negative pole, though neither acids, nor any of the common agents, showed the presence of albumen. Hence it appears that this substance may form part of an animal fluid, and yet not be discoverable by the common tests. In saliva Mr. Brande supposes that it is united with an alkali (probably soda) which, in this state of combination, loses its property of affecting vegetable colours. (Phil Trans. 1809.)

The GASTRIC JUICE is a fluid which is poured out upon the inner surface of the stomach, and is possessed of very extraordinary powers as a solvent. One of the great obstacles to an accurate analysis of it is the difficulty of procuring it sufficiently pure, and free from admixture with the contents of the stomach. It has been generally collected from animals, which have been kept, for some time before being killed, without food. In this state, it is a transparent liquor, having a saline and somewhat bitter taste, and containing neither uncombined acid nor alkali. It precipitates nitrate of silver; and, when evaporated, gives a solid residuum, which is deliquescent, and has an unpleasant smell. By the action of acids, a small proportion of albumen is discovered in it, and gelatine or mucus remains in solution. Vauquelin always found phosphoric acid in the gastric juice of herbivorous animals, whilst, on the other hand, that of man and carnivorous animals seldom gave any visible traces of free acid or alkali. The contents of the stomach, however, during the process of digestion, are almost always acid, and the particular acid, it has been shown by Dr. Prout, (Phil. Trans. 1824, p. 45.) is the muriatic, which exists not only in combination, but in a free state. In severe cases of dyspepsia, this acid is sometimes ejected from the stomach in considerable quantity. Messrs. Tiedemann and Gmelin, besides muriatic acid, find free acetic acid in the gastric juice of the dog and the horse. Butyric acid, too, has occasionally been found in the stomach of the latter animal.

This imperfect account of the properties of the gastric juice affords, it must be confessed, no explanation of the solvent power, which it exerts on all animal and vegetable substances. Even out of the body, it appears, from the experiments of Spallanzani, to retard the putrefaction of animal substances, and to reduce them to a state somewhat similar to that in which they are found after having been some time in the stomach. On substances

taken into that organ, its solvent power is even still more remarkable. In Dr. Stevens's experiments, hollow silver spheres, perforated with small holes and containing animal and vegetable food, were swallowed by a man who possessed the faculty of doing this without injury, and with the result that the food was always dissolved, and the vessel voided in an empty state. After death, it appears from the observations of Mr. Hunter, that the stomach itself is sometimes eroded by the gastric juice, large holes having been found in it from the action of that fluid. These facts, as well as the power of the gastric juice in coagulating milk, which in all animals appears to be the characteristic property of the gastric juice, are quite inexplicable on any known chemical principle.

The contents of the stomachs of animals feeding exclusively on vegetable food, even when about to pass the pylorus, and apparently fully digested, exhibit no traces of albumen. This change, Dr. Prout observes, requires the action of the pancreatic and biliary fluids, and is not distinctly visible till the food has passed some distance into the duodenum. Digestion, therefore, though begun in the stomach, is only imperfectly performed in that organ.

The PANCREATIC JUICE had not been examined with any attention, before the experiments of Tiedemann and Gmelin, who find it to differ materially from saliva, 1st. in containing twice the quantity of solidifiable matter; 2dly. in containing little mucus, and proper salivary matter, while it abounds in albumen; 3dly. in being neutral, or, at most, containing a little alkaline carbonate; 4thly. sulpho-cyanic acid does not appear to have been found in the pancreatic juice of man, and is absent from that of the sheep.

The BILE is one of those fluids, which has attracted peculiarly the notice of chemists, and which is, therefore, better understood than most others. It is to the labours of Fourcroy, and still more recently of Thenard, who has published two memoirs on the bile, that we are chiefly indebted for our knowledge of its composition. (*Mémoires d'Arcueil*, vol. i.)

The bile of the ox, from the greater quantity of it which may be procured, has been mostly the subject of experiment. Its colour is commonly yellowish green, very rarely deep green. When mixed with syrup of violets or infusion of turnsole, it produces no other change than what any other liquid of the

same colour would effect. Its taste is bitter and at the same time sweetish, and excessively nauseous. Its smell is peculiar; and something like that of melted fat. Its specific gravity is 1026; its consistence variable, from that of a thin mucilage to that of synovia. Sometimes it is limpid, and, at others, contains flocculi of a yellow matter, which may easily be separated by water.

When submitted to heat, ox-bile first deposits a portion of coagulated matter, and yields a liquid, which has the peculiar smell of bile, and which throws down a white precipitate from acetate of lead. The solid residuum has a yellowish green colour; is very bitter; somewhat deliquescent; and entirely soluble in water and in alcohol. It melts at a moderate heat, and is decomposed by a still stronger one, the products being more oil, and less carbonate of ammonia, than from animal matters in general. A very bulky coal containing several neutral salts remains in the retort. The salts extracted from this coal, taking them in the order of their quantities, are muriate of soda, phosphate of soda, phosphate of lime, and sulphate of soda. Traces, also, are discovered of oxide of iron.

The uncombined soda in bile does not exceed  $\frac{1}{100}$  its weight; and as this very minute quantity of alkali must be quite incapable of dissolving the large proportion of resin, which exists in that fluid, Thenard was induced to turn his attention to the discovery of some other solvent of resin, existing as a component of bile. Acetate of lead (the common sugar of lead of commerce) precipitates, he found, not only the resin, but the peculiar substance of which he was in search, in union with oxide of lead. But an acetate with a larger proportion of base (formed from eight parts of sugar of lead and one of litharge) produced a different effect; and precipitated only the albumen and the resin. When the remaining liquid was filtered, and the lead separated by sulphureted hydrogen gas, it gave, on evaporation, a residue, having less bitterness and considerably sweeter. In this state, the solvent of the resin could not be considered as pure, since it retained in solution a quantity of acetate of soda, arising from the decomposition, by the acetate of lead, of the salts of soda existing in the bile. He again, therefore, precipitated the solution by acetate of lead saturated with oxide, and obtained an insoluble compound of the peculiar matter and oxide of lead. This was dissolved in vinegar, the oxide of lead separated by sulphureted hydrogen, and the acid expelled by evaporation.



The substance thus obtained, to which Thenard has given the name of *picromel*, possesses the property of rendering the resin of bile easily soluble in water. Three parts are sufficient for one of the resin. The characters of *picromel* are, that it is insoluble in water and alcohol, and incapable of being crystallized; that it precipitates nitrate of mercury, and acetate of lead with excess of oxide; and that it forms, with resin and a minute quantity of soda, a triple compound, which is not decomposable by acids, nor by alkaline or earthy salts. Chevallier has shewn that it exists in human bile taken from the gall bladder after death, but he could not detect it in bile discharged by vomiting. (Ann. de Chim. et de Phys. ix. 400.) It has been analyzed by Dr. Thomson, who obtained products indicating 5 atoms of carbon + 3 of oxygen + 1 of hydrogen. (Ann. of Phil. xiv. 70.)

The resin is to be considered as the cause of the smell, and, in great part, of the colour and taste of the bile. It is solid; very bitter; and, when pure, green, but when melted it passes to yellow. It is soluble in alcohol and in pure alkalis, and is precipitable from the former by water, and from the latter by acids.

The yellow matter appears to be peculiar to the bile, and to possess characters distinct from those of other animal substances. Its presence seems to render the bile putrescent; and it is, also, the source of the concretions, which form in the gall bladders of oxen. Insoluble by itself, it becomes soluble by the intervention of soda, resin, and *picromel*; and, whatever be the solvent, it is precipitated by acids.—In the analysis of bile, the first step was to separate this yellow matter, by adding nitric acid, and to free it from the portion of resin which adheres to it. Into the remainder, acetate of lead with excess of oxide (prepared as already directed) was poured, and an insoluble compound was formed, consisting of oxide of lead and resin, from which nitric acid detached the latter in the state of soft green flakes. Sulphureted hydrogen was then passed through the liquid, which was separated by filtration from the precipitate, and evaporated to dryness. Deducting, from its weight, that of the acetate of soda, formed by the decomposition of acetate of lead, the weight of *picromel* was obtained. The saline substances were determined by calcination, lixiviation, and other common processes.

In this way, the composition of ox-bile was determined as follows;

Water .....	700. or a little more
Resin .....	24.
Picromel .....	60.5
Yellow matter .....	variable—in this case 4.
Soda .....	4.
Phosphate of soda .....	2.
Muriate of soda .....	3.2
Sulphate of soda .....	0.8
Phosphate of lime .....	1.2
Oxide of iron .....	a trace.

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300.

The bile of the dog, the sheep, the cat, and the calf, was found on analysis to be precisely similar to that of the ox. The bile of the pig, on the contrary, contained neither albumen, yellow matter, nor picromel. It consisted merely of resin in great proportion, of soda, and of salts, the nature of which has not yet been ascertained. It was entirely decomposed by acids, and even by the weakest, the acetic.

With the foregoing results of the analysis of bile, those of Prof. Berzelius are by no means in accordance. He denies the presence of resin in bile, and asserts that it is not possible to repeat the analysis of that fluid, by the processes which Thenard has described. (71 Ann. de Chim. 220.) The substance, he alleges, which, in bile, resembles resin, is precipitable by acids; and the precipitate is a compound of the acid employed with the green colouring matter of bile. When we use sulphuric acid, and apply heat, a green liquid is obtained resembling a resin; and after saturating the acid with carbonate of baryta, the green matter is soluble in water, to which it imparts its own colour and bitterness. This is the characteristic ingredient of bile, which Berzelius calls *biliary matter*. He finds bile composed of

Water .....	907.4
Biliary matter .....	80.0
Mucus of the gall bladder .....	3.0
Alkalis and salts common to all animal fluids ..	9.6

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1000.

The bile of birds contains a large quantity of albuminous matter. The picromel, which is extracted from it, is not sensibly sweet; but, on the contrary, has a sharp and bitter taste. It

contains a mere trace of soda, and does not precipitate the superacetate of lead.

In pursuing their inquiries into the function of digestion, Professors Tiedemann and Gmelin submitted bile to fresh experiments. The watery portion they state at 91.5 per cent. of the whole; the proximate animal principles, many of which are in small proportion, are cholesterine, biliary resin, picromel, osmazome, mucus, and what has been called biliary asparagin; beside other substances, not so well characterized. The salts are principally those with base of soda, viz. the margarate, oleate, acetate, cholate, bicarbonate, sulphate, and muriate, but, contrary to common opinion, no uncombined soda. The bile of the dog, though in general similar to that of the ox, contained fewer ingredients, viz. cholesterine, resin, picromel, and mucus, with various salts. Human bile, so far as their necessarily limited experience extends, furnished the same principles. After all the pains that have been taken, it must be allowed, that there is still room for fresh researches into the composition of bile, a fluid extremely complex, and made up of ingredients, many of which can be discriminated only by slight peculiarities.

HUMAN BILE was, also, an object of Thenard's researches; and his experiments, he is of opinion, have led him to as accurate a knowledge of it, as of any other species.—Its colour varies considerably; sometimes it is green, almost always brownish yellow, and sometimes it is without colour. Its taste is not very bitter. It is seldom perfectly limpid; for it generally holds suspended in it a certain quantity of yellow matter, which is sometimes even present in such quantity, as to render the bile clotted. When it is filtered, and submitted to a boiling heat, it becomes thick and emits the smell of white of egg. Evaporated to dryness, it affords an extract, which is equal to  $\frac{1}{11}$ th the weight of the bile. This extract, by calcination, affords precisely the same salts as are found in ox-bile, viz. uncombined soda; muriate, sulphate, and phosphate of soda; phosphate of lime; and oxide of iron.

All the acids decompose human bile, and precipitate from it a large quantity of albumen and of resin. These may be separated from each other by alcohol. By the application of acetate of lead, no picromel can be discovered; nor is any other ingredient found in human bile than yellow matter, albumen, resin, and saline substances. The proportions, ascertained by Thenard, are the following:

Water .....	1000.*
Yellow matter, insoluble, and floating in } the bile, a variable quantity from 2 to }	10.
Yellow matter in solution .....	<i>a trace.</i>
Albumen .....	42.
Resin .....	41.
Soda .....	5.6
Phosphates of soda and lime, sulphate } and muriate of soda, and oxide of iron }	4.5
	1100.

The yellow matter appears to be, in every respect, similar to that of ox-bile. The resin is yellowish; very fusible; very bitter, but less so, than that of ox-bile; soluble in alcohol, from which it is precipitated by water; and soluble in alkalis, from which it is thrown down by acids. In water it appears scarcely to dissolve; and yet sulphuric and nitric acids occasion a precipitate from water which has been digested on it.

If bile be submitted to the action of galvanism, Mr. Brande has found that coagulation takes place at the negative pole, where soda also appears. At the positive pole, muriatic and phosphoric acids are evolved.

The substance of the liver of the ox has been analyzed by Braconnot, but as there is nothing particularly important in the results, I content myself with referring to them. (Quarterly Journal, vii. 388.)

**BILIARY CALCULI.** The composition of biliary concretions differs in different animals. Those of the ox contain traces of bile, which is removable by the action of water, after which they are entirely destitute of taste and smell. Their colour is a yellow, of so much beauty as to render them a valuable pigment. They undergo no change at a heat below redness; but at this temperature they melt and swell, and after yielding the usual animal products, give about one-sixth their weight of a white matter which is phosphate of lime. They are nearly insoluble both in water and in alcohol; and with some difficulty in alkalis, from which they are precipitated, in green flocculi, by acids. Boiling muriatic acid takes up only a small quantity, and ren-

\* These are the numbers given by Thenard (*Mémoires d'Arcueil*, i. 57; ) but as their sum exceeds 1100, it is probable that the error will best be corrected by reducing the proportion of water.

ders them green. Hence they appear to be homogeneous; and to possess properties identical with those of the yellow matter of the bile of oxen, and of human bile.

The calculi of the human gall-bladder have been more attentively examined than those of the ox. It had been long known that they enter into fusion at a low temperature, and that the alkalis, and the fixed and volatile oils, effect their solution. One of their distinctive characters was first pointed out by Poulletier de la Salle, *viz.* that of being soluble in boiling alcohol, and precipitable, on cooling, in the form of shining scales. Fourcroy afterwards discovered several important facts respecting them, and especially their resemblance to the substance which has been already described under the name of *adipocire*.

Of the calculi examined by Thenard, only a small number was formed of white plates, crystalline and shining, and entirely adipocirous. Many consisted of yellow laminae containing from 88 to 94 *per cent.* of adipocire, and six or twelve of a colouring substance. A few were greenish on the outside, and yellow in the interior; several were covered, in spots at least, with a blackish brown crust, containing very little adipocire, but internally were like the rest. In all, excepting the perfectly white, there were traces of bile, discoverable by the action of water.—Calculi from the intestines were found to be similar to those of the gall-bladder.

It was, therefore, concluded by Fourcroy, that some of the calculi of the human gall-bladder consist entirely of adipocire; and that others are composed of the same substance, with the addition of a quantity of colouring matter, which is either yellowish or dark brown. When of the former colour, it appears not to differ from the yellow matter of the bile; and when of the latter, to be the same substance with an excess of carbon.

*Eritrogene*.—In the gall-bladder of a person who had died while labouring under jaundice, M. Bizio found a fluid possessing none of the characters of bile. The part, insoluble in water, being boiled in alcohol, gave a solution which yielded rhomboidal crystals of an emerald green colour, tasteless, and having the odour of putrid fish. The sp. gr. of the substance is 1.57; it fuses at 110° Fahr., appearing like an oil, which becomes solid on cooling. Heated up to 212°, it volatilizes,

giving a purple vapour, from whence its name. It has several other remarkable properties, for which, as it has hitherto been recognized in only one instance, I refer to the Quart. Journ. xvi. 173.

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### SECTION III.

#### *Of Milk, Eggs, and Chyle.*

The milk is a fluid, which is secreted by animals of the class *Mammalia*, for the nourishment of their young. Though differing considerably in the different species of animals, yet it admits of the following general description :

It is an opaque liquid, of a white colour, with sometimes a slight tinge of blue or yellow. Its taste is sweetish and grateful; but varies occasionally, as does its colour also, with the food of the animal. Its specific gravity is variable; that of cows' milk, according to Brisson, being about 1020, and that of ewes' milk 1040.

The milk may be resolved, partly by standing, and partly by agents that do not essentially alter the nature of its components, into three proximate ingredients, the cream, curd, and whey.

1. The cream rises, as is well known, to the surface of milk after it has stood for some hours; and the proportion may be ascertained by a very simple instrument, proposed by Mr. Johnson. It consists of a glass tube, 10 inches long, graduated into 100 equal parts, into which the recent milk is to be put, for spontaneous separation of the cream. (Thomson's Annals, x. 304.) Cream has many of the properties of an oil; is smooth and unctuous to the touch; and stains cloth in the same manner as other fat substances. By standing for some days, it becomes gradually thicker, and at length forms a soft solid, in which the flavour of cream is no longer perceived, and that of cheese is substituted in its place. Cream, of the specific gravity 1.0244, is composed, according to Berzelius, of

Butter .....	4.5
Cheese .....	3.5
Whey .....	92.0

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100.

But, as 92 parts of whey contain 4.4 of sugar of milk and salts, it follows that cream contains 12.5 per cent. of solid matter.

When cream is agitated, as is done by the common process of churning, it separates into two parts, a thick animal oil, well known by the name of butter, and a fluid which possesses exactly the same properties as milk that has been deprived of its cream. This change has been supposed to be owing to the combination of the cream with the oxygen of the atmosphere; but it takes place, though perhaps not equally well, in vessels from which the air is excluded.

Butter has generally a yellow colour and a soft consistence. Its specific gravity is inferior to that of water. At the temperature of  $96^{\circ}$  or  $98^{\circ}$ , it melts, and when kept in this state for some time, a portion both of whey and curd separates from it. Its transparency is thus increased, but its taste is, at the same time, rendered less agreeable. In this state, however, it may be kept longer without becoming rancid; and it is not improbable that it is in part by combination with the whey, that salt contributes to the preservation of butter. Butter, therefore may be considered as an animal oil, united with a portion of whey and of curd. This oil, according to Chevreul, is resolvable into stearine and two distinct oils; the one, soluble in all proportions in cold alcohol, and containing several kinds of acid, he calls *butirine*, to which fresh butter owes its yellow colour and odour; the other agrees in its properties with elain, not, however, free from other principles, as butyric acid, a colouring and odorous matter, &c. (Ann. de Ch. et de Ph. xxii. 366.)

Butter may be saponified, by treating it with above one-third of its weight of pure potassa. The soapy mass thus produced, decomposed by tartaric acid, affords a saponified fat, and a watery liquid. The latter contains beside bitartrate of potassa, butyric, caproic, and capric acids, and glycirine. The three acids are volatile, and may be separated by distillation: they may be separated from each other by the different solubilities of the salts, which they compose with hydrate of baryta.

When milk, either deprived or not of its cream, is mixed with certain substances, or even allowed to stand till it becomes sour, it undergoes a change which is called coagulation, consisting in its separation into a solid substance termed curd, and a fluid called whey. This change may be effected by several

agents; by all acids, and by many neutral salts; by gum, sugar, and certain vegetable juices; by the gastric fluid; and especially by the infusion of the inner coat of a calf's stomach, called *rennet*. The precipitation by acids, Scheele has explained by supposing that they form, with the curd, a combination which requires more water for solution than milk contains; (Essays, p. 267,) and accordingly the curd is found always to contain a portion of that acid, by which coagulation has been produced. But, in other cases, the coagulation cannot be thus accounted for; and is, indeed, altogether inexplicable. Thus the infusion of a piece of calf's stomach, not larger than half a crown, coagulates a quantity of milk sufficient for making a cheese of sixty pounds' weight; although the quantity of coagulating matter cannot in this case exceed a few grains. (Holland's Cheshire Report, p. 268.)

The curd of milk, when pressed, salted, and partly dried, composes cheese. In good cheese, however, there is always a large proportion of butter, which is enveloped in the curd, and is not afterwards easily separable. Curd, therefore, for exhibiting its chemical properties, should be prepared from milk which has been deprived of cream, and should be made by the intervention of rennet. It is a white solid substance, insoluble in water and in alcohol, but readily soluble in pure alkalis, and precipitable therefrom by acids, though in a state more like tallow than the original curd. During solution in alkalis, a strong smell of ammonia is produced; and hence curd appears to be converted, by their action, into volatile alkali and fat. Liquid ammonia also dissolves curd, and it appears to be soluble by the pure alkaline earths. From the resemblance of its properties to those of the coagulated white of an egg, Scheele was induced to regard cheese as identical with albumen; and it is not improbable that, if the curd could be obtained perfectly pure, their properties would exactly agree. By the combustion and calcination of curd, it appears, however, to afford a larger proportion of phosphate of lime and other saline substances, than is obtained from the coagulated white of an egg.

Berzelius found that the ashes, obtained by incinerating cheese, amount to 6.5 per cent. of its weight. The ash consists chiefly of earthy phosphates, with a little pure lime; but contains neither alkali, nor oxide of iron. Cheese, digested with



muriatic acid, loses its earthy phosphates, and afterwards burns away without leaving any ash. The presence of so large a quantity of the earthy phosphates, in the most nutritious part of milk, may be regarded, Berzelius justly observes, as a wise provision of nature; and peculiarly adapts milk to the nutrition of young animals, in whose economy there exists the greatest demand for the earthy phosphates, for the purpose of ossification.

Cheese is generally considered as insoluble in water; but if it be precipitated from milk by sulphuric acid, then well pressed, and digested with carbonate of baryta, cheese affords with water a yellowish solution resembling a solution of gum. The solution boiled in an open vessel becomes covered with a white pellicle, precisely as milk does, and acquires the smell of boiled milk.

Cheese produces, with the mineral acids, the same combinations as albumen and fibrin, though its neutral compounds are less soluble than those of fibrin. A great excess of acetic acid is required to dissolve cheese, and the neutral compound formed with this acid appears to be insoluble. When it has not been completely separated from butter, this floats upon the surface of its solution in acetic acid. Alcohol converts cheese into an adipocirous and foetid substance.

In addition to the substances before found in cheese, Proust has discovered two new ones, *viz.* a combustible acid and a combustible oxide, both of which he believes to be the produce of the fermentation of the curd. They may be obtained as follows:—The curd of milk is to be kept several days under water, and then put into a bottle containing water enough to cover it a few inches, the mouth being closed by a small plate of glass. No gas is evolved; but acetic, phosphoric, and *caseic* acids are produced, all saturated with ammonia, which is generated at the same time. The fluid may be withdrawn, and replaced by fresh water, when the same changes will go on as before. These washings, evaporated in a silver basin and left to stand a few days, solidify into a saline mass slightly transparent, and tasting strongly of cheese. The three salts already mentioned are to be dissolved by alcohol, and the solution boiled with carbonate of lead. The phosphoric acid, forming an insoluble salt, is thus separated; and the mixture of caseate

and acetate of lead is to be decomposed by sulphureted hydrogen. The two acids remaining in solution are separated from each other by distillation, the acetic only being volatile.

*Caseic acid* is of the colour and consistence of syrup; reddens litmus paper; and has an acid bitter taste mixed with that of cheese. It concretes, on standing, into a granular transparent mass like honey. It does not affect lime water, muriate of tin, or acetate of lead. It precipitates the oxides of silver, gold, and mercury, but not the oxides of metals that more strongly attract oxygen. With infusion of galls, it produces a thick white precipitate. Nitric acid converts it into oxalic acid, forming at the same time a little benzoic acid and some of the yellow bitter principle.

*Caseate of ammonia* has a sharp saline bitter taste mixed with that of cheese, to which indeed it appears chiefly to communicate flavour. It always contains an excess of acid, and is not crystallizable.

*The caseous oxide* remains after the action of alcohol on the saline mass before described, constituting a bulky white powder. It is to be purified by washing with water till deprived of all cheesy taste; and afterwards by boiling in water, filtering, and evaporation, during which the oxide forms films on the surface, which are to be separated, washed, and dried. It is almost tasteless, soft to the touch, crumbles under the fingers, and when pressed hard, has a peculiar greasy feel. It begins to dissolve in water at  $140^{\circ}$ . Hot alcohol dissolves very little, and it separates on cooling in crystalline grains. It is insoluble in ether, but disappears rapidly in liquid potassa.

Caseous oxide occurs frequently in cheese in detached points, and forms those small particles, which affect the teeth like an earthy and dry substance. The oxide and caseate of ammonia together constitute from 30 to 35 per cent. of good cheese. (Quarterly Journ. vii. 391.)

The experiments of Braconnot on the caseous acid and oxide (Ann. de Ch. et de Ph. Oct. 1827,) have led him to deny the existence of the former, and to consider the caseate of ammonia of Proust as a compound of various substances, flavoured with a yellow pungent oil. He admits, however, the existence of caseous oxide, and regards it as a highly-azotized animal principle, not peculiar to cheese, but produced by the

putrefaction of all animal substances. He proposes, therefore, to discontinue its name, and to apply to it that of *aposepidine*, from *απο* and *σηπεδων*, (product of putrefaction.)

The **WHEY**, or liquid which remains after the separation of all the curd, is a thin and almost transparent fluid, of a yellowish green colour and a pleasant sweetish taste. It still contains, generally, a portion both of curd and of butter; the former of which may be separated by a boiling heat, in the form of a coagulum. The buttery matter, also, separates by heat, especially if the whey be previously allowed to become sour. (Cheshire Report, page 262.) Whey contains, indeed, in its recent state, some uncombined acetic acid.

When whey which has been deprived, as much as possible, of the butter and curd, is slowly evaporated, it yields the substance already described under the name of sugar of milk. Besides this substance, it contains, also, several saline bodies, *viz.* muriate of potassa, phosphates of lime and of iron, and sulphate of potassa; and a peculiar animal matter, which gives a precipitate with infusion of galls, and affords carbonate of ammonia by distillation. Sour whey contains an acid long supposed to be a peculiar one, and called the *lactic*. This, however, is now found to be essentially the acetic, modified by holding some animal matter in combination.

From this account of the composition of milk, several properties of the entire fluid may be understood. When fresh milk is boiled, its albuminous part is not coagulated into a mass like the white of an egg, on account of the large quantity of water through which it is diffused; but a thin pellicle forms on the surface, which, if removed, is immediately replaced by another; and thus the whole of the albumen may be separated in successive portions. If the pellicle fall to the bottom, it becomes burnt, and gives the milk a peculiar flavour.

In order to procure butter from milk, it is not necessary, in the first place, to separate the cream; for butter may be obtained at once by the churning of milk, and has then the name of milk-butter. It is inferior, however, to butter made from cream, in consequence of its containing a larger proportion both of whey and of curd.

Milk is susceptible of the vinous fermentation, and is employed by the Tartars in making a sort of wine, which they call *Koumiss*. (37 Phil. Mag. 6.) It is prepared chiefly from

mares' milk, and has an agreeable sweetish taste. By distillation, it yields a considerable quantity of alcohol. What is most remarkable with respect to this fermented liquor is, that it does not appear to owe its origin to the saccharine part of the fluid; for Fourcroy and Vauquelin have found that milk, after fermentation, yields as much sugar of milk as before.

There appears to be a considerable difference in the quality of the milk of different animals. Human milk is sweeter than that of cows, and yields a larger proportion of cream; but from this the butter cannot be separated by agitation. It deposits, also, a part of its curd by mere repose. Asses' milk bears a stronger resemblance to human milk than to any other. The cream, however, is in small quantity, and yields a soft, white, and nearly tasteless butter. The curd is so abundant as even to separate on standing, before the milk becomes sour. Goats' milk yields a remarkably thick and unctuous cream, and abounds also in curd. The milk of sheep bears a strong resemblance to that of cows, and yields a large proportion of curd of a fat and unctuous kind. Mares' milk is thin and insipid, and affords very little cream, from which it is very difficult to separate any butter by agitation.

The constituents of skimmed cows' milk are stated by Berzelius as follows:

Water . . . . .	928.75
Cheese, with a trace of butter . . . .	28.00
Sugar of milk . . . . .	35.00
Muriate of potassa . . . . .	1.70
Phosphate of potassa . . . . .	0.25
Lactic acid, lactate of potassa, and a trace of lactate of iron . . . . .	6.00
Earthy phosphates . . . . .	0.30
	<hr/>
	1000.

#### *Of Eggs.*

Eggs were attentively examined by Dr. Prout, (Phil. Trans. 1822), in the course of an inquiry into the changes that occur during incubation. The specific gravity of new laid eggs was found to vary from 1.080 to 1.090. By long keeping, they become specifically lighter than water, in consequence of the substitution of a quantity of air for the water which escapes through their pores. They suffer also a great loss of weight,

amounting on an average to little short of a grain per day. Of an egg weighing 1000 grains, the shell constitutes about 106 grains, the white 604, and the yelk 290, or thereabouts.

Eggs lose a little of their weight by being boiled, and the water becomes impregnated with about 0.3 grains of saline matter from an egg of common size. This saline fluid is found on evaporation to be strongly alkaline, and to contain also animal matter, sulphuric and phosphoric acids, chlorine, lime, magnesia, and carbonates of those earths, all which substances exist both in the white and the yelk.

The shell contains about 2 per cent. of animal matter, with 1 per cent. of phosphates of lime and magnesia, the rest being carbonate of lime with a little carbonate of magnesia. Vauquelin found, also, in the burnt shells, traces of iron and sulphur.

The yelk of the egg, besides the more common ingredients of animal fluids, contains a considerable portion of uncombined phosphorus; which, when the dried yelk is burnt, forms a glassy coating of phosphoric acid, that effectually defends the charcoal from combustion. In the white of eggs, which, as has been already stated, consists chiefly of albumen, sulphur exists in a free state, and by combustion becomes, as Berzelius has remarked, changed into sulphuric acid. The yelk communicates to heated alcohol a deep yellow colour, and, on cooling, crystals of a sebaceous matter are deposited, and a portion of a yellow semi-fluid oil. On distilling off the alcohol, the oil may be obtained separate. In one instance, the yelk, weighing 316.5 grains, contained 170.2 water, 55.3 albumen, and 91 yellow oil; but these proportions varied in different instances. The proportions of the saline matter, both of the white and yelk, to each other, appear liable, also, to considerable variation.

#### *Of Chyle.*

The chyle has been examined by Mr. Brande, who obtained it from the thoracic duct of an animal, about four hours after taking food. If taken at a longer interval, it is mixed with a greater or less proportion of lymph. When unmixed with blood, it has the following properties:

1. It is an opake fluid of a perfectly white colour, without smell, and having a slightly salt taste, accompanied by some degree of sweetness.

2. It does not affect the colour of litmus or turmeric, but it slowly changes violet paper to green.

3. Its specific gravity somewhat exceeds that of water, but is less than that of blood.

4. In about ten minutes after being taken from the duct, it assumes the appearance of a stiff jelly, which, in the course of 24 hours, separates into two parts, producing a firm and contracted coagulum, surrounded by a transparent colourless fluid. Its spontaneous changes, indeed, bear a striking resemblance to those which take place in blood.

The coagulated portion has a closer resemblance to the cheese of milk than to fibrin. It is rapidly dissolved both by pure and subcarbonated alkalis, forming pale brown compounds. Its solution in liquid ammonia is of a reddish hue. The acids throw down a substance intermediate between fat and albumen, which an excess of nitric acid redissolves in the cold; and sulphuric, muriatic, and acetic acids, by boiling for a short time, also dissolve it.

Sulphuric acid, diluted, dissolves the coagulum, unless the water be increased to six times the weight of the acid. Alkalis do not precipitate the solution. It is transparent, of a pale brown colour, and, after the addition of alkali, is decomposed by infusions of tan.

When the coagulum is kept some weeks in one part of nitric acid, and 15 of water, it is converted into *adipocire*. Muriatic, acetic, and oxalic acids, dissolve the coagulum; but neither citric nor tartaric acids have any action on it.

The serous part of the chyle, when heated, becomes slightly turbid, and deposits flakes of albumen. The clear liquid, by evaporation to half its bulk, deposits crystals, bearing a strong resemblance to sugar of milk. They are soluble in 20 parts of water at 60° Fahrenheit, or in four of boiling water, and the taste of the solution is extremely sweet. By nitric acid, they are converted into a white powder, having the properties of *saccholactic acid*, as described by Scheele.

The destructive distillation of the serous part of chyle afforded a minute quantity of charcoal, with traces of phosphate of lime, and of muriate and carbonate of soda.

From these experiments, it appears that chyle bears a striking analogy to milk, not only in its external appearance,

but in chemical properties and composition. It must be acknowledged, however, that the results, which have been described, are not perfectly coincident with those obtained by Emmert and Vauquelin, each of whom submitted to analysis the chyle of the horse. Emmert was unable to discover the smallest trace of sugar of milk; (80 Ann. de Chimie, 81,) and Vauquelin found also, 1st, a large proportion of albumen; 2d, a smaller one of fibrin; 3d, a fatty substance, which gives to the chyle the appearance of milk; and 4thly, several salts, such as potassa, muriate of potassa, and proto-phosphate of iron. (81 Ann. de Chimie, 113.) Berzelius, also, appears to distrust the analogy between chyle and milk. (View of Animal Chemistry, p. 74.)

The most recent examinations of the chyle are by Drs. Marcet and Prout, who compared the chyle from two dogs, the one exclusively fed on animal, the other on vegetable food. Their results are contained in the following Table. (Ann. of Phil. xv. 25.)

	Vegetable Food.	Animal Food.
Water .....	93.6	89.2
Fibrin .....	0.6	0.8
Incipient albumen? ....	4.6	4.7
Sugar of milk? .....	a trace	—
Oily matter .....	a trace	trace
Saline matters .....	0.8	0.7
	100.	100.

#### SECTION IV.

*Of the Mucus of the Nose; the Tears; the Humours of the Eye; and the Liquor of Surfaces and of Cavities, &c.*

1. *The mucus of the nose* was examined by Fourcroy and Vauquelin, in the state in which it is discharged during catarrh. Its principal qualities appear to be owing to the large proportion, which it contains, of the substance termed by Dr. Bostock animal mucus. By exposure to the air, this substance becomes viscid; but, when recently secreted, its consistence does not appear to be thicker than that of tears. It contains,

beside other neutral salts, a small proportion of carbonate of soda; and hence it precipitates the solutions of baryta and of lime. Water does not dissolve it, and it can only be brought into a state of diffusion by agitation. The acids thicken it, when used in small quantity; but in a larger proportion they dissolve it. Pure liquid alkalis decompose it, and extricate ammonia. Chlorine renders it thick and dry; and reduces it to a state almost resembling parchment.

Berzelius found the mucus of the nose to consist of

Water .....	933.7
Mucous matter .....	53.3
Muriates of potassa and soda .....	5.6
Impure lactate of soda .....	0.9
Albumen and animal matter, insoluble in water, but soluble in alcohol ..	} 3.5

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1000.

2. The *tears* appear to differ from the mucus of the nose in no respect, except in being of a more fluid consistence. They are perfectly pellucid, have a saline taste, and a specific gravity rather greater than that of water. They change the colour of syrup of violets to green, owing to their containing a portion of uncombined soda. Mr. Hunter found that when tears are exposed to a temperature of  $160^{\circ}$ , a coagulum is formed, and that a substance still remains in solution, which is coagulable by Goulard's extract of lead. These properties indicate the presence both of albumen and of mucus. By evaporation, the tears afford a yellow extract, which is insoluble in water, but is readily soluble in alkalis. Sulphuric acid disengages, from this extract, both carbonic acid and muriatic acid gases. After its combustion, phosphate of soda and phosphate of lime are also discovered in it. Fresh tears are decomposed by chlorine, and a precipitate is thrown down in flakes, which resembles the matter obtained by evaporation. Tears, therefore, are composed of water; an animal fluid resembling albumen; another fluid which is probably mucus; and various neutral salts.

3. *The humours of the eye.*—The aqueous humour is a clear transparent liquid, of the specific gravity 1009. It has little smell or taste, and scarcely affects blue vegetable colours. By evaporation it leaves a residuum, amounting to about 8 per



cent. Boiling occasions a slight coagulation; and tan precipitates it, both before and after being heated. Nitrate of silver precipitates muriate of silver from it, but no other metallic salts affect it. Hence it may be inferred, that the aqueous humour consists of a large proportion of water; and of albumen, gelatine, and several neutral salts.

The vitreous humour agrees with the aqueous as to the nature of its ingredients, and differs only in their proportion. In the crystalline lens, both albumen and gelatine are present in considerably larger quantity. It is soluble in cold water; but the solution is coagulated by heat, and by the addition of tan. Its specific gravity is nearly 1100.—It appears, therefore, that all the humours of the eye are composed of the same ingredients, and differ only in the proportion which they bear to each other.

A recent analysis of the humours of the eye by Berzelius, has determined their composition as follows:

	Aqueous Humour.	Vitreous Humour.
Water .....	98.10	98.40
Albumen .....	a trace	0.16
Muriates and lactates ....	1.15	1.42
Soda with animal matter } soluble in water .... }	0.75	0.02
	100.	100.

The lens of the eye was found to be composed of

Water .....	58
Peculiar matter .....	35.9
Muriates, lactates, and animal matter soluble } in alcohol .....	2.4
Animal matter soluble only in water .....	1.3
Insoluble membrane .....	2.4
	100.

In the ashes of the crystalline lens, Berzelius found only minute traces of iron; but in those of the black matter which covers the choroid coat, he discovered a large proportion of the oxide of that metal. (Ann. de Ch. et de Ph. v. 51.)

4. *Liquor of surfaces.*—On the surface of every cavity throughout the body a fluid is constantly poured out, in sufficient quantity to lubricate the parts; and occasionally, also, to

keep certain cavities in a state of distension. To this head may be referred the fluid which moistens the pleura and the peritonæum, and the contents of the pericardium, of the ventricles of the brain, and of the amnios. It is only a part of these, however, that have been accurately examined.

The liquor of the pericardium has been analyzed by Dr. Bostock. It had the appearance of the serum of the blood; and when exposed to the heat of boiling water, became opaque and gelatinous. By slow evaporation it left a residuum equal to  $\frac{1}{13}$  of the whole. It was precipitated by bi-chloride of mercury; after the action of which, infusion of galls had no effect, but a copious sediment was produced by Goulard's extract. From these characters, Dr. Bostock is disposed to consider it as a compound of albumen and mucus with muriate of soda and water, but without any gelatine. (Nicholson's Journal, xiv. 147.) The following proportions he assigns as approximations:

Water . . . . .	92
Albumen . . . . .	5.5
Mucus . . . . .	2
Muriate of soda . . . . .	0.5
	<hr/>
	100.

The liquor of the amnios, or the fluid which surrounds the fœtus, is stated by Vauquelin and Buniva to be remarkable, in the cow, for affording a peculiar acid, already described under the name of the amniotic; but Dr. Prout, who has since examined this liquor with much attention, was not able to detect any such principle. (Thomson's Ann. v. 471.) The liquor, on which he made his experiments, had the sp. gr. 1.013. Its taste was bland and sweetish like fresh whey; and, when concentrated by evaporation, it yielded crystals of sugar and milk. It consisted of.

Water . . . . .	977
Albumen . . . . .	2.6
Substance soluble in alcohol . . . . .	16.6
Saline substances and sugar of milk . . . . .	3.8
	<hr/>
	1000.

In the human subject, the composition of the liquor of the amnios is entirely different; none of the amniotic acid appearing

to exist in it. The only ingredients, that are found in it, are albumen, gelatine, with a portion of muriate and carbonate of soda, and some phosphate of lime. It is precipitated by heat, by acids, by alcohol, and by infusion of galls.

5. *Lymph*.—The fluid found in the thoracic duct of animals that have been kept 24 hours without food, is perfectly transparent and colourless, and seems to differ, in no respect, from that which is contained in the lymphatic vessels. Its properties are described by Mr. Brande as follows :

(a) It is miscible in every proportion with water.

(b) It produces no change in vegetable colours.

(c) It is neither coagulated by heat, by acids, nor by alcohol, but is rendered slightly turbid by the last-mentioned agent.

(d) It gives, on evaporation, a very sparing residuum, which turns the colour of violet paper green. By incineration, this matter gives a very little muriate of soda, but no iron.

(e) When submitted to electrical action, there was an evolution of alkali, and a separation of albumen, at the negative pole. At the positive wire, muriatic acid only seemed to be evolved.

6. *Pus*.—Pus is the fluid secreted by an inflamed surface, generally towards the close of the inflammation. It is of a yellowish white colour, and of the consistence of thick cream ; has the sp. gr. 1.031 to 1.033 ; is insipid and inodorous when cold ; and when examined by the microscope, exhibits white globules swimming in a transparent fluid. It produces no change on vegetable colours in its recent state, but becomes acid on exposure to the air.

Pus is not easily miscible with water, and when agitated with it, the pus sinks to the bottom on standing. Diluted sulphuric acid does not act upon it, but concentrated sulphuric, muriatic, and nitric acids dissolve it. Alkaline solutions form with it a whitish ropy fluid, which is precipitated on adding water. Pure ammonia changes it to a transparent jelly, and dissolves a considerable proportion of it.

Pus yields a white precipitate with nitrate of silver, and a still more copious and flaky one with nitrate and with bi-chloride of mercury. Its characters appear, however, to be liable to several modifications, which are described by Dr. Pearson in the *Phil. Trans.* for 1810. The criteria proposed for distinguishing pus from mucus, Dr. Pearson did not find at all satisfactory ; but

the following has since been proposed by Grassmeyer. Triturate the fluid to be tried with an equal quantity of warm water; then add to it an equal portion of a saturated solution of sub-carbonate of potassa; and set the mixture aside. If it contain pus, a transparent jelly subsides in a few hours, but this does not happen if only mucus be present. (Thomson's Chemistry, iv. 584.)

7. *Synovia*.—This fluid, which is found in the cavities of the joints, may, from its office of lubricating the parts in which it is found, be described in this place, though in composition it differs considerably from the liquor of surfaces. It is at first a viscid liquid, but soon becomes gelatinous; and, after remaining some time in this state, again assumes a fluid form, and deposits a fibrous matter. Alcohol separates from it a portion of albumen, but the remaining liquid remains viscid. Acetic acid destroys its viscosity, and precipitates a quantity of white threads, which have a striking resemblance to vegetable gluten. The same substance is precipitated by the mineral acids, but not unless they are diluted with a large quantity of water; for in their concentrated form, they have the power of dissolving it. By continuing the analysis, several neutral salts may be obtained, and the proportions of the entire fluid have thus been stated by Margueron. (Ann. de Chim. xiv.)

Fibrous matter .....	11.86
Albumen .....	4.52
Muriate of soda .....	1.75
Soda .....	0.71
Phosphate of lime .....	0.70
Water .....	80.46

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100.

8. *The fluid of perspiration, or sweat*, has been examined by Berzelius; but under the disadvantage of operating on a very small quantity. A few drops, collected and evaporated on a watch-glass, left a yellowish residue, having all the appearance, under the microscope, of the usual mixture of muriates of potassa and soda with lactic (impure acetic) acid, lactate of soda, and its accompanying animal matter. It reddened litmus, and dissolved in alcohol; and was, without doubt, of the same nature as the analogous matter found in other animal fluids.

Dr. Bostock, who had lately an opportunity of examining about 4 ounces of the fluid of perspiration, agrees generally with Berzelius and Thenard, but could discover no uncombined acid. Of the animal matter, a portion dissolved in alcohol, and partook of the characters of urea and osmazome. The part insoluble in alcohol most nearly resembled, in sensible and chemical qualities, the principal ingredient of the serosity of the blood. Albumen was but just appreciable, and there was no evidence of the presence of gelatine. It contained, beside a trace of phosphates and sulphates,

Water .....	981.70
Animal matter .....	4.60
Muriate of soda .....	12.56
Soda .....	1.14

1000. (Med.Ch.Tr. xiv. 424.)

## SECTION V.

### *Of the Urine and Urinary Calculi.*

The urine, though one of the most complicated fluids of the animal body, containing at least a dozen different substances, is perhaps one of those, the composition of which is now best understood. For a long period of time, the attention of chemists seems to have been limited to the extraction of phosphorus and neutral salts from urine; but a new direction was given to their labours by the valuable discoveries of Fourcroy and Vauquelin. (Ann. de Ch. xxxi. 48.) The analysis of the urine has been prosecuted, also, with great success in this country by Cruickshank (Phil. Mag. ii. 249); in Spain by Proust (Ann. de Chim. xxxvi. 258); and more recently by that indefatigable philosopher, Professor Berzelius of Stockholm. (Thomson's Annals, ii. 416.) And though some important facts have been contributed by other persons, yet it is chiefly to these writers that we are indebted for the materials of its chemical history.

The external properties of the urine need no description; and indeed none would apply universally to a fluid, which is constantly varying, not only in the diseased but in the healthy

state of the body. The quantity, voided in each diurnal period, is of course greatly modified by circumstances. Haller states it at 49 oz. ; Dr. Bostock at 40 oz. ; and Dr. Prout at 32 oz. or 2 lb. avoirdupois on the average of the whole year. The following account of its chemical properties is to be understood, as applying to the urine which is voided early in the morning, or at least several hours after a meal. In this state it has a deep yellow colour, and an intensely bitter taste. Its specific gravity is variable. Dr. Bryan Robinson fixes it at 1030, water being 1000 ; and Mr. Cruickshank found it to vary from 1005 to 1033. From my own experiments, I am disposed to consider the number stated by Dr. Robinson as a fair general average.

The substances, which appear to me to have been satisfactorily proved to exist in healthy urine, are the following :

- |                                 |                                   |
|---------------------------------|-----------------------------------|
| 1. Water.                       | 12. Lactate (acetate) of ammonia. |
| 2. Free phosphoric acid.        |                                   |
| 3. Phosphate of lime.           | 13. Sulphate of potassa.          |
| 4. ————— magnesia.              | 14. ————— soda.                   |
| 5. Fluoric acid.                | 15. Fluuate of lime.              |
| 6. Uric acid.                   | 16. Muriate of soda.              |
| 7. Benzoic acid.                | 17. ————— ammonia.                |
| 8. Lactic (impure acetic) acid. | 18. Phosphate of soda.            |
| 9. Urea.                        | 19. ————— ammonia.                |
| 10. Gelatine.                   | 20. Sulphur.                      |
| 11. Albumen.                    | 21. Silica.                       |

The presence of an uncombined acid in urine is shown by its invariably, when recently voided, reddening blue vegetable colours. This effect is owing partly to the phosphoric, and partly to the lactic and uric acids, which urine contains. Berzelius imagines that the weakest acids are those which are most likely to remain unsaturated, and to produce this effect on vegetable colours ; but Dr. Prout is inclined rather to believe that the uric acid in urine is united with ammonia, and that mineral acids cause a precipitation from urine by saturating the ammoniacal base. The reddening effect he is disposed to ascribe to the super-phosphate of ammonia.

The lactic (impure acetic) and phosphoric acids form the solvent, by which the phosphate of lime is retained in solution ; and, if this portion of acid be saturated, the earthy phosphate is precipitated. A few drops of pure ammonia, added to recent

urine, occasion a white cloud; and a sediment of neutral phosphate of lime falls, in the proportion of about 2 grains from 4 oz. of urine. If lime-water be mixed with urine, a still larger quantity of phosphate of lime is deposited; for the newly-added earth unites with the free phosphoric acid, and a quantity of phosphate of lime is generated, in addition to that which before existed in solution. In the precipitate, formed by either of these processes, a small proportion of magnesia is discoverable, which existed, no doubt, in combination with phosphoric acid. The sediment contains, also, according to Berzelius, fluuate of lime. The presence of the last-mentioned substance was ascertained by adding sulphuric acid, which set at liberty vapours of fluoric acid, in sufficient quantity to corrode glass. (*Ann. de Chim.* lxi. 256; and Thomson's *Annals*, ii. 416.)

When the urine has stood for twenty-four hours at a mean temperature, the uric acid, urate of ammonia, and phosphate of lime are in a great measure deposited; and still more speedily and completely, if the urine be first evaporated to half its bulk. They may be separated from each other, either by diluted nitric acid, which leaves the uric acid, and takes up only the phosphate of lime; or by calcining the mixture in a red-heat, which destroys the uric acid, but not the calcareous phosphate. By this operation, the uric acid is found to vary considerably; but the phosphate of lime is pretty constantly in the proportion of a grain from 2 ounces of urine. The quantity of uric acid obtained from urine is greatly increased, by adding to that fluid almost any other acid, and allowing it to stand for some days; at the end of which time small crystalline grains will be found lining the inner surface of the vessel. (*Egan, Phil. Mag.* xxiii. 298.)

The existence of salts, containing sulphuric acid, in urine, is proved by adding muriate of baryta, to urine acidulated with muriatic acid. This excess of acid prevents the precipitation of the phosphates, which would otherwise be decomposed by the barytic salt. From the weight of the precipitate, Berzelius computes that the proportion of sulphuric acid in urine exceeds that of phosphoric acid.—If nitrate of baryta, with an excess of nitric acid, be employed, and if the urine, after depositing the sulphate of baryta, be evaporated, a further portion of sulphate of baryta is deposited in small hard crystals. Now the sul-

phuric acid, which occasions this *second* production of the barytic sulphate, must have been *formed* during evaporation; and can only be accounted for by supposing, that a portion of sulphur, existing in the urine, has been acidified by the excess of nitric acid.

The muriates of potassa and soda occur both in blood and in urine, and hence appear to pass the kidneys unchanged. Their presence in the latter fluid may be shown by first precipitating the phosphates and sulphates with nitrate of baryta, and then adding nitrate of silver. A copious precipitation in this case never fails to be produced.

When urine, which has deposited its phosphate of lime and uric acid, is submitted to distillation, a liquid condenses in the receiver, which has a very peculiar and nauseous smell, and effervesces strongly with acids, in consequence of its containing carbonate of ammonia. In the retort there remains a residuum, which, if evaporated to the consistence of honey, composes from  $\frac{1}{24}$  to  $\frac{1}{36}$  the weight of the urine. When a little of this extract is added to a quantity of nitric acid, diluted with an equal weight of water, a number of shining white or yellowish scales are deposited, resembling the boracic acid, and in the proportion of  $\frac{5}{8}$  or  $\frac{7}{8}$  the weight of the extract. This precipitate is occasioned by the action of the nitric acid on the urea which is contained in urine; and to the decomposition of the same substance is owing the carbonate of ammonia, obtained from urine by distillation. (See the Section on Urea.)

From the extract of urine, the peculiar substance, called urea, may be separated by digesting the extract repeatedly with alcohol, and decanting the solutions, which are to be gently evaporated. Its proportion varies very considerably; but it has been stated, by Mr. Cruickshank, at about  $\frac{1}{70}$  the weight of the urine, or one-half that of the inspissated extract. The undissolved residue contains lactic (impure acetic) acid and a number of neutral salts, consisting of muriate of potassa, muriate of soda, phosphate of soda, and phosphate and lactate of ammonia. Muriate of ammonia is, also, occasionally found, and is dissolved, along with the urea, by the alcohol. These salts admit of being separated from each other by solution and evaporation. The muriates, at a certain degree of concentration, form a pellicle, which is to be removed while the liquor is hot. The solution,



when cold, deposits two sets of crystals; rhomboidal prisms, which are the phosphate of ammonia; and rectangular tables, consisting of phosphate of soda.

Along with the urea, a portion of benzoic acid is, also, taken up by the alcohol. The presence of this acid in urine may be shown, by evaporating it to the consistence of syrup, and pouring in muriatic acid; when a precipitate appears, which consists of benzoic acid. In human urine its proportion is small, and Berzelius could not even discover a trace of it in the urine of children, in which Scheele states that he found it; but in that of herbivorous quadrupeds, so large a quantity exists as to be worth extraction. On the average, Vauquelin has shown that it forms about  $\frac{1}{300}$  of the urine of this class of animals. (Annales de Chimie, lxi. 311.)

If human urine be evaporated to the consistence of syrup, and alcohol be added, the substance remaining undissolved is acid. This acid combines with ammonia, and the compound is soluble in alcohol. From this solution the ammonia is disengaged by lime; and from the new salt thus formed, the lime may be precipitated by oxalic acid, which leaves the *lactic acid* dissolved in water. By this process, a small part only of the lactic acid is obtained from urine; the greater portion of it being dissolved by the alcohol, together with the lactate of ammonia. It has already been stated (p. 448), that the lactic acid is nothing else than the acetic, modified by its combination with animal matter. Proust, indeed, obtained acetic acid by distilling fresh-made extract of urine with sulphuric acid. By diluting the residuum of this distillation, when beginning to grow thick, with a large quantity of cold water, and saturating the excess of an acid with an alkali, a resinous matter resembling castor was produced.

Albumen, gelatine, and mucus exist, also, in healthy urine, but in very variable proportion. When urine is heated nearly to the boiling temperature, a white flocculent precipitate often forms in it. This is in part phosphate of lime, thrown down by the ammonia resulting from the decomposition of urea; but it also contains coagulated albumen, which remains after adding muriatic acid to dissolve the calcareous phosphate. In dropsy, the proportion of albumen is often sufficient to produce a distinct coagulation both by heat and acids. Gelatine is dis-

covered, on adding infusion of galls, by a precipitate which amounts, according to Mr. Cruickshank, to  $\frac{1}{40}$  part the weight of the urine. The presence of an excess of albumen in urine is the characteristic symptom of a disease described by Dr. Prout (on Calculous Diseases, p. 37.) But in general he considers the albuminous part of urine as more nearly allied in properties to that found in chyle than to that of blood. It often exists, when the urine is not coagulable by heat; but in this case it may be discovered by the delicate test of triple prussiate of potassa, aided by a few drops of acetic acid.

Mucus is suspended in all newly evacuated urine, and affects its perfect transparency. If the urine be voided in different portions, the mucus, which naturally lines the urinary passages, is most abundant in the first, and less so in the subsequent portions. When recent urine is filtered, the mucus remains on the filter, in the form of transparent and colourless flocculi. The cloud, which appears in the urine during fever, is merely this mucus, which subsides more slowly than usual, in consequence of the increased specific gravity of the urine. From urine, filtered when warm, a greyish white sediment falls in cooling, which gradually acquires a reddish hue and a crystalline form. The greyish powder is soluble in caustic potassa, without any evolution of ammonia; but, as it becomes red and crystallized, potassa disengages ammonia from it in abundance. Berzelius considers it, therefore, as super-urate of ammonia. The deposit is partly soluble, also, in acetic acid, which extracts a substance having the characters of mucus. There appears, indeed, to be an affinity between uric acid and mucus; for that acid separates most abundantly from urine, which has not been deprived of mucus by filtration. In some diseases of the bladder, its mucous secretion appears to undergo a considerable change, and to assume a purulent appearance. (Berzelius, in Thomson's Annals, ii. 420.)

Sulphur was first discovered in urine by Proust. This fluid, he observes, blackens silver vessels in which it is evaporated, and scales are detached which consist of sulphuret of silver. Sulphureted hydrogen gas, he finds also, is disengaged from urine which has been kept about fifteen days; a remark which has since been made also by Vogel. But the greatest part of the sulphur in urine is united with oxygen in the state of sulphuric acid, which is combined with different bases.

The same distinguished chemist (Proust) supposed that he had discovered carbonic acid in urine, by examining the air bubbles which ascend from this fluid during ebullition. There can be little doubt, however, that the carbonic acid, thus evolved, arises from the decomposition of urea by the increased temperature. Vogel, however, has been led to the same conclusion (93 Ann. de Ch. 71), and Mr. Brande considers it to be established by the escape of carbonic acid from urine, when placed under an exhausted receiver. Dr. Marcet, too (on Calculus, p. 159), admits that, under certain circumstances, urine may contain carbonic acid. To the same source (urea), may be referred the carbonate of lime, found by Proust on the surface of casks in which urine had been kept. By the decomposition of urea, carbonate of ammonia is formed; and this, reacting on the phosphate of lime contained in urine, will doubtless compose carbonate of lime. The occasional presence of the sulphate of soda rests on better evidence; for it frequently happens that only a part of the precipitate, formed by adding muriate of baryta to urine, is dissolved by muriatic acid; thus indicating the formation of sulphate of baryta.

The colour and smell of urine, Berzelius ascribes to the lactic acid accompanying animal matters; but Dr. Prout conceives that, in some cases, it is owing to the presence of alkaline purpurates. On adding pure and white urate of ammonia to healthy urine, he found the urate always to acquire a colour like that of uric acid calculi, till a certain quantity had been added, when it ceased to acquire colour on adding more. This can only be explained by supposing that urine contains two colouring matters, one of which has an affinity for urate of ammonia, the other not.

Berzelius discovered siliceous earth in urine by treating extract of urine, first with alcohol, then with water, and finally with muriatic acid. The silica remained in the form of a grey powder, which, by fusion with soda, became glass. Its source he apprehends to be in the water which we drink, which almost universally contains silica.

With regard to the proportion of the different ingredients of urine, Berzelius finds that it differs essentially in the same individual, even from causes which have little influence on health. The following Table may be considered as showing its average composition :

Water .....	933.00
Urea .....	30.10
Sulphate of potassa .....	3.71
————— soda .....	3.16
Phosphate of soda .....	2.94
————— ammonia .....	1.65
Muriate of soda .....	4.45
————— ammonia .....	1.50
Free lactic (acetic) acid .....	} 17.14
Lactate (acetate) of ammonia .....	
Animal matter soluble in alcohol and accompanying the lactates .....	
Animal matter insoluble in alcohol ....	
Urea not separable from the above ....	
Earthy phosphates with a trace of fluete of lime .....	} 1.00
Uric acid .....	
Mucus of the bladder .....	0.32
Silica .....	0.03
	<hr/> 1000.

The uric acid is extremely variable in quantity; but in the particular instance, which furnished the above results, it was so copious as to be deposited on cooling. The earthy phosphates contain 11 per cent. more magnesia, than exists in the earth of bones, or in the ashes of blood. Much more potassa is discoverable, also, in urine and in milk, than in blood.

Acidification, it has been ingeniously suggested by Berzelius, is the chief healthy office of the kidneys. It is in those organs, that the sulphur and phosphorus, present in blood, are converted into sulphuric and phosphoric acids, and that a new acid, the uric, is generated. In some diseases, the acidifying tendency is carried to excess, and nitric and oxalic acids are generated, the former of which probably converts a part of the uric acid into purpuric; and the latter, uniting with lime, composes oxalate of lime. In other cases, the acidifying process is suspended, and unchanged blood or albumen; neutral substances, as sugar or urea; and even alkalis, as ammonia, lime, or magnesia, are abundantly separated, the sulphur and phosphorus, at the same time, escaping unacidified. When acids are formed in excess, the urine is scanty and high coloured, and the character

of the disease is inflammatory. When neutral or alkaline substances are redundant, the urine is pale and copious, and the disease is accompanied with irritation or debility. (See Prout on Calculus.)

The putrefaction of urine is attended with a series of changes, somewhat analogous to those accompanying its distillation. The urea, which it contains, is decomposed and converted into carbonate of ammonia, which neutralizes all the redundant acids, and precipitates phosphate of lime. At the same time, the ammonia, uniting with the phosphate of magnesia, composes a salt, which settles in white crystals on the inner surface of the vessel. This salt is the ammoniaco-magnesian phosphate, which constitutes so large a part of some urinary calculi. The albumen and gelatine contained in the urine also undergo decomposition, and flakes are deposited, which consist of both these substances. Acetic acid is generated, and becomes saturated with ammonia. Acetate and carbonate of ammonia, and the ammoniaco-magnesian phosphate, appear, therefore, to be the principal substances generated by the putrefaction of urine.

Some important facts have been ascertained by Mr. Cruickshank, respecting the changes that the urine undergoes in different diseases. In dropsy, the urine was coagulated so completely by heat and by acids, as to differ but little from the serum of the blood. When this disease, however, arose from a morbid state of the liver, the urine was not coagulable; but was observed to be small in quantity, high coloured, and to deposit a considerable portion of pink sediment (probably the *substance rosacée* of Proust.) In inflammatory affections, the urine was found to be loaded with albumen. In gout, towards the end of the paroxysm, the urine deposited a lateritious sediment, which consisted of a very minute quantity of uric acid, a larger quantity of phosphate of lime, and some peculiar animal fluid not soluble in water. The urine of jaundiced persons contained a small quantity of bile, which was discoverable by the addition of muriatic acid. Hysterical urine was remarkable for a larger proportion of saline ingredients, but had scarcely any animalized matter.

The composition of the urine differs essentially in the different classes of animals. Urea appears to be a constituent of the urine of all animals, so far as it has hitherto been examined; but the uric acid is not found in herbivorous quadrupeds, the

urine of which contains, instead of it, a large proportion of benzoic acid. That of the horse and of the rabbit are remarkable for becoming milky after being voided, in consequence of the deposition of carbonate of lime. The urine of the rabbit contains, also, carbonates of magnesia and potassa, and sulphates of potassa and lime. The urine of the cow, besides a larger proportion of benzoic acid, holds in solution carbonate and sulphate of potassa and muriate of potassa.—The urine of domestic fowls, which is voided through the same passage as the excrement, was found by Fourcroy and Vauquelin, and more lately by Chevreul, to contain uric acid. And Dr. Wollaston has determined the proportion of uric acid to be greatest, in the urine of birds that feed on animal food. In the hawk, fed on flesh only, it was remarkably abundant; and the gannet, feeding solely on fish, discharged no solid matter except uric acid. (Phil. Trans. 1810.) The uric acid, combined with ammonia, has been found, also, by Dr. Prout, to constitute upwards of 90 per cent. of the excrement of an animal, belonging to a different class, the serpent called *boa constrictor*. (Thom. Ann. v. 413.) Mr. Brande, some years ago, discovered it in the urine of the camel. But, on the other hand, Vauquelin has proved that it is entirely absent from the urine of the lion and tiger, though fed on flesh, and though their urine abounds in urea. (82 Ann. de Chim. 199.)

URINARY CALCULI.—Connected with the analysis of urine is that of the concretions, which are found in the bladder, and which occasion a disease, equally formidable from its symptoms, and its surgical treatment. Little was known respecting their chemical composition, till the time of Scheele; to whose genius we owe on this, as on many other subjects, the first, and therefore the most difficult steps towards accurate analysis. By the discovery of the *uric* (or, as he termed it, *lithic*) acid in one of the most common varieties of calculus, and in the ordinary urine, he paved the way to every thing that has been since ascertained, respecting other varieties; and his experiments have been most ably followed up by those of Dr. Wollaston, and of Fourcroy and Vauquelin. It is but justice to Dr. Wollaston, however, to state, that the principal distinctions of the several species of calculus were pointed out by him in the Philosophical Transactions for the year 1797, in a memoir not less distinguished by the importance of its facts, than by the clearness and simplicity

with which they are narrated. Two years afterwards, the experiments of Fourcroy and his associate were communicated to the National Institute; so that the title to priority unquestionably belongs to our own countryman. Several valuable additions have been since made to our knowledge of the subject by Dr. Pearson, Mr. Brande, and others; and an excellent history of all that was before known, combined with much original matter, has been contributed by Dr. Marcet, in a separate volume, entitled "An Essay on the Chemical History and Medical Treatment of Calculous Disorders." 8vo. London. In the plates which are annexed to that work, will be found the most exact representations of the several varieties of urinary concretions, that have yet been published. A great deal of important information respecting the chemical history of the urine, and of the concretions formed from it, may be found also in Dr. Prout's "Inquiry into the Nature and Treatment of Gravel, Calculus," &c. For the statistical history of the disease, the reader may consult with advantage several essays dispersed through the volumes published by the Medico-Chirurgical Society of London, and Dr. Yelloly's paper in the Philosophical Transactions for 1829.

The ingredients of urinary calculi are much less numerous than those of the urine. The following appear to be the substances, which most frequently occur in concretions of this sort, *viz.*, uric or lithic acid alone, and united with ammonia; phosphate of lime; ammoniaco-magnesian phosphate; muriate of ammonia (Yelloly, Phil. Trans. 1829); oxalate of lime; silica; and an animal matter, which serves the purpose of a cement to the earthy ingredients. To these, Proust added the carbonate of lime (Ann. de Chim. xxxvi.); and its presence in some cases has been lately fully demonstrated. (Phil. Trans. 1829, p. 79.) The ingredients of rarer occurrence are the *cystic oxide* of Dr. Wollaston, and the *xanthic oxide* of Dr. Marcet. It is scarcely ever that any of these substances is found singly. Nevertheless, the predominance of some one of them gives to the concretion its peculiar characters; and determines the genus to which it should be assigned. Several arrangements of urinary calculi have been proposed. Fourcroy and Vauquelin have enumerated three genera, which they have divided again into no less than twelve species. In these subdivisions, however, several minute differences have been attended to, which are scarcely sufficient

grounds for specific distinctions ; and it appears to me sufficient for every purpose of arrangement to class them under the following heads :

I. Calculi which are chiefly composed of uric acid or urate of ammonia :

II. Calculi principally composed of the ammoniaco-magnesian phosphate :

III. Calculi consisting, for the most part, of phosphate of lime :

IV. Calculi containing principally carbonate of lime :

V. Calculi which derive their characteristic property from oxalate of lime ; and

VI. Calculi composed of an animal oxide, *viz.* of the substance called *cystic oxide*, or of the *xanthic oxide*.

I. The calculi consisting entirely of *uric acid* are of very rare occurrence ; but those, in which it prevails, and gives the character of the species, form a very considerable proportion, perhaps one half, of urinary concretions. Calculi of this kind are of various sizes, from that of a bean to that of a large egg. Their shape is most commonly a flattened oval ; but when more than one are found, they acquire, by friction against each other, several sides and angles. The best view of their internal structure is obtained by sawing them through their longest and widest diameter, when they exhibit generally a central nucleus, of more compact texture, and greater hardness and lustre, than the rest of the stone ; but generally of the same figure. From this to the circumference, a number of distinct layers are perceived ; and these layers, when the calculus is broken, exhibit a radiated structure, the radii converging towards the centre. The harder varieties, when divided by the saw, admit of some degree of polish, and bear a considerable resemblance to wood. Their colour is various, but generally of different shades of yellow, from pale straw-yellow to a deep shade of that colour, approaching to brown or sometimes brown with a mixture of red. Their specific gravity, according to Fourcroy, varies from 1.276 to 1.786 ; but generally exceeds 1.500.

The chemical characters of calculi of this kind resemble those of the uric acid. When burned in a crucible, they emit the smell of horn, and are almost entirely consumed ; a black dense coal remaining, which amounts to about  $\frac{1}{5}$ th the weight of the calculus. They dissolve, either wholly or in great measure, in



solutions of pure potassa and pure soda, and are precipitated again by acids. A very striking property of this sort of concretions is, that when a few grains are heated on a watch-glass, with a small quantity of nitric acid, and the mixture cautiously evaporated to dryness, a beautiful red substance remains, which dissolves in water and tinges the skin of the same colour.

The *red sand*, voided occasionally in considerable quantity, and constituting one of the forms of the disease called *the gravel*, is uric acid very nearly pure. It is probably liberated from urate of ammonia by a free acid generated in the kidneys, just as it is precipitated by adding any acid to urine recently voided. The acid precipitating gravel in the kidneys may be either the phosphoric, nitric, or purpuric. (Prout, p. 127.)

The *urate or lithate of ammonia* calculus is generally of a clay colour, with a smooth and sometimes tuberculated surface. It is composed of concentric layers, and its fracture is very fine earthy, resembling that of compact limestone. It is small, and, in its pure state, rather uncommon; but urate of ammonia often occurs with uric acid forming a mixed calculus.

In chemical characters, it closely resembles the last species. Before the blow-pipe, however, it decrepitates strongly; but it was found by Dr. Yelloly, not to part with its ammonia when heated to 440° Fahr. It is much more soluble in water than uric acid calculus, and always emits a smell of ammonia with caustic potassa. It readily dissolves also in alkaline sub-carbonates, which the uric species does not. (Prout, p. 84.) Muriate of ammonia appears to be a frequent ingredient of this kind of concretion. (Phil. Trans. 1829, p. 74.)

II. The *ammoniaco-magnesian phosphate*, or *triple calculus*, is scarcely ever found without an admixture of some other substance, especially of phosphate of lime. Calculi of this sort are easily discriminated from those of the first species, by their colour, which is white, generally pure white. They attain a much greater size than uric acid calculi; and, in one or two instances, have increased so as to fill the whole capacity of the bladder. The layers are distinguishable only by different degrees of hardness and density; and small cells are often formed by the interrupted deposition of these layers, which are lined with sparkling crystals. The calculi of this kind are soft, and their powder dissolves sufficiently in the mouth, to give a distinct sweetish

taste. The same substance is sometimes voided, also, in the state of gravel, constituting perfectly white shining crystals.

Boiling water acts upon the ammoniaco-magnesian phosphate; and the calculus loses about  $\frac{4}{10}$  of its weight, which is deposited, on cooling, in the form of shining crystals. When exposed to heat it first becomes black, emits a smell of ammonia, and a white powder is left, which fuses imperfectly when the heat is more strongly urged. Most acids (even the acetic, and sulphuric acid diluted to the specific gravity 1.020) dissolve it rapidly, and deposit it again on the addition of alkalis. Pure alkalis do not dissolve it, but disengage ammonia. To extract the phosphoric acid, Dr. Wollaston dissolved the calculus in acetic acid, and precipitated the phosphoric acid by an excess of acetate of lead. To the clear liquor, sulphuric acid was added, which threw down the excess of lead, and, at the same time, formed sulphate of magnesia. Evaporation to dryness removed the acetic acid; and, by raising the heat, the sulphate of ammonia and excess of sulphuric acid were expelled; leaving the sulphate of magnesia pure, and capable of forming crystals by solution and evaporation.

III. The third species of calculus, composed chiefly of *phosphate of lime*, is usually, on its outer surface, of a pale brown colour, and so smooth as to appear polished. When sawed, it is found to be regularly laminated, and the layers adhere so slightly, as to be readily separated into concentric coats. Internally the colour is white, but not of that pure and brilliant kind which distinguishes the ammoniaco-magnesian phosphate. The small crystals, also, which occur in the former variety, are never found in this; and its powder, when rubbed between the fingers, is considerably more harsh and rough.

The phosphate of lime calculus dissolves, though slowly, in diluted nitric, muriatic, and acetic acids (but not in sulphuric acid of the specific gravity 1.020), and is precipitated unchanged by alkalis. A small fragment put into a drop of muriatic acid, on a piece of glass over a candle, is soon dissolved; and, when the acid is evaporated, crystallizes in needles, which make angles of  $60^\circ$  and  $120^\circ$  with each other. This property Dr. Wollaston considers as a very delicate test of the phosphate of lime. When exposed to the blow-pipe, it first blackens, but soon becomes white, and, by intensely urging the flame, may at length be fused. When the phosphate of lime and ammoniaco-

magnesian phosphate exist together, they compose a calculus, a fragment of which may be melted with great ease by the blow-pipe into a vitreous globule; and which has therefore been called by Dr. Wollaston, the *fusible calculus*. This calculus, when pulverized and acted upon by very weak acetic acid, is only partially dissolved, the ammoniaco-magnesian phosphate being taken up by the acid, and the phosphate of lime left. In this way, it is easy to approximate the proportion of the two phosphates.

IV. *Carbonate of lime* has been found, though rarely, composing small, perfectly white, and very friable calculi. This was the appearance of some examined by Dr. Prout. Dr. Gilby of Clifton has detected it in four instances, and Mr. Smith, of Bristol, has related another, in which calculi, composed chiefly of carbonate of lime held together by animal mucus, were taken from the bladder of a boy. (Medico-Chir. Trans. xi. 14.) These calculi, however, had nearly the colour of mulberry calculi.

V. Calculi of the fifth kind, though their composition was not ascertained, have been long distinguished from others, by the peculiarities of their external characters, under the name of *mulberry calculi*. This epithet has been derived from their resemblance to the fruit of the mulberry. They are usually of a much darker colour than the other varieties, and are covered, generally, with a number of projecting tubercles; but the species comprehends, also, some perfectly smooth concretions of a pale colour. Their hardness greatly exceeds that of the other kinds; for it is not easy to reduce them to powder by scraping with a knife. They have also a greater degree of specific gravity, varying, according to Fourcroy, from 1.428 to 1.076.

Calculi of this species, when pulverized, are soluble in muriatic and nitric acids; but not unless the acids are concentrated and heated. The solution by muriatic acid has a deep brown colour, but deposits white crystals on cooling. Pure alkalis do not decompose this variety of calculus; but when it is digested with alkaline carbonates, the oxalic acid is separated, and replaced by carbonic acid. To exhibit the oxalic acid in a separate state, the oxalate of potassa may be decomposed by acetate of baryta or super-acetate of lead, and the oxalate of lead or baryta by sulphuric acid. This is the process of

Fourcroy; but Dr. Wollaston disengaged the oxalic acid by the direct addition of sulphuric acid to the pulverized calculus, and the crystallization of the acid which was thus detached.

The presence of lime, in this variety of calculus, is demonstrated, in a very simple manner, by burning it in a crucible, and strongly calcining the residuum, or by exposure to the blow-pipe. By the addition of water, we obtain lime-water.

Silica is a very rare ingredient, and has been discovered in calculi, in one or two instances only.

VI. A new species of calculus from the human bladder was discovered, by Dr. Wollaston, about the year 1805. It appears to be extremely rare; for in 1810, when its properties were first described in the *Philosophical Transactions*, only two instances of it had occurred to its discoverer. With the assistance of Dr. Wollaston's clear and accurate description, and of the proper experiments, I have recognised two other examples, in a collection of calculi now in my possession; and Dr. Marcet has since detected it in no less than three instances. Professor Stromeyer, too, has discovered it in gravel from the human body; and Lassaigne found it to constitute 97.5 per cent. of a calculus extracted from the bladder of a dog. (*Ann. of Phil. N.S. vi. 316.*)

In external appearance, these calculi resemble more nearly the triple phosphate of magnesia than any other sort of calculus; but they are more compact, and do not consist of distinct laminæ, but appear as one mass, confusedly crystallized throughout its substance. They have a yellowish semi-transparency, and a peculiar glistening lustre, like that of a body having a high refractive density.

Under the blow-pipe, the new calculus gives a peculiarly fetid smell, quite distinct from that of uric acid. Distilled in close vessels, it yields fetid carbonate of ammonia, partly solid and partly fluid, and a heavy fetid oil; and there remains a black spongy coal, much smaller in proportion than from uric acid calculi.

It is so readily acted upon by chemical agents, that its characters are best taken from an enumeration of the few feeble powers which it can resist. These are water, alcohol, acetic, tartaric, and citric acids, and saturated carbonate of ammonia; all which are incapable of dissolving it, except in very minute proportion. Its solvents, on the other hand, are

far more numerous. It is abundantly dissolved by muriatic, nitric, sulphuric, phosphoric, and oxalic acids; by potassa, soda, ammonia, and lime-water; and even by fully saturated carbonates of potassa and soda. When, therefore, it is intended to separate it from acids, the carbonate of ammonia is best adapted to the purpose; and, for the same reason, the acetic and citric acids are best suited to precipitate it from alkalis.

Its combinations with acids crystallize in slender spiculæ, radiating from a centre, which readily dissolves again in water. Its compounds with alkalis form small granular crystals. Lassaigne, who has investigated its acid compounds, has also analyzed it by combustion with peroxide of copper, and found it to consist of

Carbon .....	36.2
Azote .....	34.0
Oxygen .....	17.0
Hydrogen .....	12.8
	100.

As this substance does not affect vegetable colours, and has all the chemical habitudes of an oxide, Dr. Wollaston distinguishes it by the name of *cystic oxide*. This name it is not worth while to alter, though Dr. Marcet has lately met with instances, in which its origin may be clearly traced to the kidneys and not to the bladder.

Amongst the urinary calculi examined by Dr. Marcet were two, the properties of which were found to differ from those of every known species. The first was of a reddish or cinnamon colour; was soluble in acids, though less readily than in alkalis; and gave with nitric acid a solution which, when evaporated to dryness, had the remarkable property of assuming a bright lemon colour. It was distinguished from cystic oxide, by being much less soluble in acids; and, from uric acid, by considerably greater solubility in water. From the colour which it affords with nitric acid, Dr. Marcet has applied to it the term of *xanthic oxide*, from  $\xi\alpha\upsilon\theta\omicron\varsigma$  (*yellow*).

The other calculus exhibited a train of properties, corresponding exactly with those of fibrin; and should other examples of a similar kind occur, they may be distinguished, Dr. Marcet thinks, by the epithet *fibrinous calculi*. (Essay, &c. chap. iv.)

Such are the principal kinds of urinary concretions. If any addition were made to the five classes, under which they have been arranged, I would propose to add two others; the sixth comprehending those calculi, which contain several of the foregoing ingredients, in such a state of admixture as not to be distinguishable without chemical analysis; and the seventh those, in which the different substances are disposed in distinct layers or in concentric strata. It may be proper, however, to give an outline of the classification proposed by Fourcroy and Vauquelin, after the analysis of more than 600 of these concretions.

GENUS I.—CALCULI COMPOSED CHIEFLY OF ONE  
INGREDIENT.

- Species* 1. Calculus of uric acid.  
 2. ———— urate of ammonia.  
 3. ———— carbonate of lime.  
 4. ———— oxalate of lime.

GENUS II.—CALCULI COMPOSED OF TWO INGREDIENTS.

- Species* 1. Calculus of uric acid and earthy phosphates in distinct layers.  
 2. ———— of uric acid and earthy phosphates intimately mixed.  
 3. ———— of urate of ammonia and the phosphates in layers.  
 4. ———— of the same ingredients intimately mixed.  
 5. ———— of earthy phosphates mixed, or else in fine layers.  
 6. ———— of oxalate of lime and uric acid in distinct layers.  
 7. ———— of oxalate of lime and earthy phosphates in layers.

GENUS III.—CALCULI COMPOSED OF THREE OR FOUR  
INGREDIENTS.

- Species* 1. Calculus of uric acid or urate of ammonia, earthy phosphates, and oxalate of lime.  
 2. ———— of uric acid, urate of ammonia, earthy phosphates, and silica.

The urinary concretions, which have been extracted from

the bladders of inferior animals differ from those of the human subject in containing no uric acid, and in consisting, for the most part, of carbonate and phosphate of lime, cemented by animal matter. Carbonate of magnesia, also, has been found in the urinary calculi of herbivorous animals. (Ann. de Chim. et de Phys. xxii. 440.)

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## SECTION VI.

### *Of Bones, Shells, Crusts, Horn, and Cartilage.*

The bones of animals are composed partly of earthy salts, which give them solidity and hardness, and partly of animal matter, which serves the purpose of a cement, and keeps the earthy ingredients together. By long-continued boiling, a large part of the animal matter is extracted, and a solution is obtained, which concretes, on cooling, into a gelatinous mass. Hence bones contain gelatine as one of their ingredients. But besides this animalized substance, another is discovered by the slow action of diluted nitric or muriatic acid. Either of these acids dissolves both the earthy salts and gelatine; and a soft flexible substance remains, retaining, in a great measure, the shape of the original bone. This soft and spongy substance seems to be analogous to cartilage; and is essential to the constitution of all organized bones and shells. Its production appears to be the first step in the formation of bone, and of the other hard coverings of animals. In chemical composition, it has been found by Mr. Hatchett (to whom we owe its discovery) most to resemble coagulated albumen.

Besides the marrow, which is lodged in the hollow cavities of bones, they contain, in the most hard and solid part of their substance, a proportion of oil. This oil makes its appearance in a hard and suety form, on the surface of the gelatinous mass extracted by boiling. It exudes, also, from the bones of recent anatomical preparations; and a portion of it passes over, in a separate but altered state, when bones are submitted to distillation. By this process, bones are deprived, not only of their oily part, but the other animal substances which they contain are decomposed; a quantity of carbonate of ammonia is generated; and in the retort there remain the earthy ingredients blackened by charcoal. By a farther combustion in the open

air, this charcoal is destroyed; and the earthy ingredients are left in a perfectly white state. In this way large quantities of bones are distilled for the sake of the carbonate of ammonia, which is afterwards applied in making the muriate of ammonia. The animal oil (formerly used in medicine, under the name of *Dippel's oil*) is now, on account of its offensive smell, which unfits it for most other purposes, chiefly converted into lamp-black.

When diluted muriatic or nitric acid is poured upon the white ashes of bones, an effervescence takes place, and nearly the whole is dissolved. Solution of pure ammonia, added to the filtered liquid, precipitates a white earth in great abundance; but, after it has ceased to produce any effect, the addition of carbonate of ammonia occasions a fresh precipitation. What is thrown down by the pure alkali is composed of phosphate of lime and a small quantity of phosphate of magnesia; and the precipitate by the mild alkali is the carbonate of lime. The proportions, deduced from the analysis of ox-bones by Fourcroy and Vauquelin, are the following :

Animal matter . . . . .	51
Phosphate of lime . . . . .	37.7
Carbonate of lime . . . . .	10
Phosphate of magnesia ..	1.3
	<hr/>
	100.

Human bones were found by Fourcroy and Vauquelin, who have given a good general formula for the analysis of bones (72 Ann. de Chim. 282), to contain some iron and manganese, and a larger proportion of magnesia than exists in the bones of herbivorous quadrupeds. This, indeed, might have been expected from the large quantity of magnesia, which is constantly passing off in human urine, but not in that of other animals. Alumine and silex were also found, by the same chemists, in human bones. Hildebrandt, however, has lately analyzed human bones, without being able to discover magnesia in them. (83 Ann. de Chim. 199.)

Besides the above ingredients, Mr. Hatchett discovered in bones a minute quantity of sulphate of lime; and Berzelius has detected a combination of fluoric acid with the same earth, which Morocchini had previously found in enamel. Berzelius has



given the following tabular view of the results of his analysis (Annales de Chimie, lxi. 257) :

	Dry Human Bones.	Enamel of Human Teeth.	Dry Ox Bones.	Enamel of Ox Teeth.
Cartilage . . . . .	32.17	.. —	33.30	.. 3.56
Blood-vessels . . . . .	1.13	.. —	—	.. —
Fluate of lime . . . . .	2.0	.. 3.2	.. 2.90	.. 4.0
Phosphate of lime . . . . .	51.04	.. 85.3	.. 55.45	.. 81.0
Carbonate of lime . . . . .	11.30	.. 8.0	.. 3.85	.. 7.10
Phosphate of magnesia . . . . .	1.16	.. 1.5	.. 2.05	.. 3.0
Soda, muriate of soda, } water, &c. . . . . }	1.20	.. 2.0	.. 2.45	.. 1.34
	100.	100.	100.	100.

Human teeth are composed of the same ingredients as the enamel, and in the same proportion, except that in addition to other ingredients, they contain cartilage. This cartilaginous basis Mr. Hatchett found to remain in the original shape of the tooth, after removing the other component parts by diluted nitric acid. The enamel, on the contrary, dissolves entirely in diluted nitric acid, and is, therefore, free from cartilage. But it probably contains gelatine, and to the solution of this animal substance (which is not afterwards precipitable by alkalis) may perhaps be ascribed the loss, which forms part of the following results of the analysis of enamel obtained by Mr. Pepys. He found the enamel of human teeth to consist of

Phosphate of lime . . . . .	78
Carbonate of lime . . . . .	6
Loss and water . . . . .	16
	100

The substance of the teeth Mr. Pepys found to be composed as follows :

	Roots of the Teeth.	Teeth of Adults.	First Teeth of Children.
Phosphate of lime . . . . .	58	64	62
Carbonate of lime . . . . .	4	6	6
Cartilage . . . . .	28	20	20
Loss . . . . .	10	10	12
	100	100	100

The shells, with which several marine and also some land animals are covered, have been divided by Mr. Hatchett into

and it is soluble, except the cellular texture of veins and nerves, in acetic acid. By boiling it becomes, like the fibrin of blood, insoluble in acetic acid, and imparts to the water, with which it has been boiled, a constituent part (*osmazome*), which has a strong and pleasant taste of flesh, and cannot be gelatinized. When this is dissolved, and mixed with the uncoagulated part of the humours of the flesh, it forms what is called *broth*, the strength and taste of which depend, not only on the dissolved gelatine of the cellular texture, but also on the fibrin, the taste of which it retains. The taste does not depend on the extractive matter of Thouvenel; for flesh, from which this extract has been separated, still gives a palatable though colourless soup.

Considerable differences exist in the colour and other properties of the muscular flesh of different animals; but the cause of these differences is not well understood. It depends, most probably, on the proportion which the fibrin, albumen, and other principles bear to each other. Gelatine appears to be most abundant in the flesh of young animals; and albumen and extract in that of old ones.

The *tendons*, or *sinews*, as they are commonly called, are the strong cords in which muscles terminate, and which connect them with the bones. They differ from muscle in the total absence of fibrin; and in being completely soluble in water by sufficiently long boiling. The solution has the properties of gelatine.

The *ligaments* are excessively strong bands, which tie the bones together at the different joints. They are in a great measure, but not completely, soluble by boiling water; and contain, therefore, beside gelatine, some other animal substance, probably coagulated albumen.

*Membranes* are thin semi-transparent substances, which sometimes form bags for containing fluids, and sometimes line the different cavities of the body. They are for the most part, though not entirely, soluble in water; and are composed, therefore, chiefly of gelatine. Hence by the common process of tanning, membranes are convertible into leather. There is an essential difference, however, between cellular or serous membranes, and mucous membranes. The latter furnish no gelatine by boiling; and are sooner destroyed than any animal substance, the brain excepted, by maceration in water, or by the action of acids.

## SECTION VIII.

*Of the soft Coverings of Animals, viz., Nails, Scales, Skin, Hair, Feathers, and Wool.*

The *nails* and *hoofs* of animals most nearly resemble horn in chemical composition. Their basis seems to be a series of membranes composed of coagulated albumen, in which is deposited a quantity of gelatine. Long boiling does not entirely dissolve them. By calcination they leave only a very small proportion of earthy matter.

The *scales* of serpents also resemble horn in their chemical composition and properties. The scales of fish, on the contrary, are more nearly analogous to mother-of-pearl, and are composed of alternate layers of membrane and phosphate of lime.

The *skin* consists of two distinct parts, a tough white membrane on the outside, which is almost insensible, and an internal one, full of blood-vessels and nerves, and distinguished by great sensibility. Between these two, in the human body, is a soft mucous substance called *rete mucosum*.

1. The external layer, called the *cuticle*, or *epidermis*, is best separated from the parts beneath by the action of epispastics on the living skin. It is not soluble in water, nor in acids, unless they are sufficiently concentrated to decompose it. Hence it differs from gelatine. Alkalis however dissolve it; and, in this respect, it agrees with coagulated albumen, which it resembles, also, in receiving a yellow tinge from nitric acid.

2. The *cutis vera*, which lies beneath the cuticle, consists of a number of fibres crossing each other in various directions, and has considerable firmness and elasticity. Long-continued boiling in water entirely dissolves it, and a solution is obtained which gelatinates on cooling, or, by farther evaporation, may be wholly converted into glue.

The true skin is composed, therefore, almost entirely of gelatine; but under some modification which renders it insoluble in water. It is this substance that adapts the skins of animals for two important uses, that of being converted into leather by the reception of the tanning principle, and that of furnishing glue.

3. Of the *rete mucosum* very little is known. It is that part of the skin, on which its colour depends; and by the sufficiently

long-continued application of chlorine gas, it has been found that in the negro it may be entirely, but not permanently, deprived of its colour.

*Hair* has been examined with considerable attention by Vauquelin. He effected a complete solution of it in water by using a Papin's digester. The application of the proper temperature required, however, some caution; for if raised too high, the hair was decomposed and gave carbonate of ammonia, empyreumatic oil, and sulphureted hydrogen. The solution always contained a sort of bituminous oil, the colour of which approached to that of the hair which had been dissolved. After separating this oil, the solution was precipitated by infusion of galls and by chlorine; but did not gelatinate on cooling. Acids occasioned a precipitate, which was redissolved by adding more acid. Silver was precipitated from its solutions of a black colour, and lead of a brown.

A diluted solution of potassa dissolved hair, excepting a little oil, sulphur, and iron; and the compound was a sort of soap. The oil, if red hair was employed, had a yellow tinge. Alcohol, also, extracted from hair a portion of oil, the colour of which varied with that of the hair.

The coal, obtained by incinerating hair, afforded phosphate, sulphate, and carbonate of lime, muriate of soda, silica, magnesia, and oxides of iron and manganese. The whole of these substances bore a very small proportion to the hair, and varied in hair of different colours. Hair, therefore, appears to consist chiefly of an animal matter resembling coagulated albumen; of an oil of various colours; of sulphur, silica, carbonate and phosphate of lime; and oxides of iron, and manganese.

*Feathers* probably agree in composition with hair. The quill, Mr. Hatchett has shown, consists of coagulated albumen without any gelatine.

*Wool* has not been so much the subject of experiment, as from its great importance it deserves. What is known respecting it may be found in Bancroft's and Berthollet's Treatises on Dyeing. When growing upon the sheep, it is enveloped in a soapy matter, from which it requires to be cleansed before it is manufactured.

Braconnot has shown that by the action of sulphuric acid, wool is converted into the peculiar substance called *leucine*. The ultimate analysis of wool has been performed by Dr. Ure, who finds it to consist of

Carbon . . . .	10 atoms . . . .	60 . . . . .	55.00
Oxygen . . . .	4 do. . . . .	32 . . . . .	29.40
Hydrogen . . .	3 do. . . . .	3 . . . . .	2.80
Azote . . . .	1 do. . . . .	14 . . . . .	12.80
		109	100.

*Silk*, the production of various species of caterpillars, and used as the soft covering of the insect during its chrysalis state, is in fine threads, covered with a sort of varnish. This varnish is soluble in boiling water, but not in alcohol; it resembles gelatine in being precipitable by tan and muriate of tin, but differs from it in other respects. It may be separated also from silk by soap, and by soap leys. It amounts, according to Roard, to 23 per cent. of the weight of the silk. (Ann. de Chim. lxxv.) Raw silk, also, contains a portion of wax, which dissolves in boiling alcohol, and separates as the alcohol cools.

Silk cleansed from these substances has been but imperfectly examined. It is insoluble both in water and in alcohol, but dissolves in pure alkalis and concentrated acids. By the action of nitric acid, it yields the peculiar substance described under the name of the *bitter principle*.

Dr. Ure submitted the bleached fibres of silk to decomposition by peroxide of copper, and obtained the following results. (Phil. Trans. 1822.)

Carbon . . . .	10 atoms . . . .	60 . . . . .	50.8
Oxygen . . . .	5 do. . . . .	40 . . . . .	34.
Hydrogen . . .	4 do. . . . .	4 . . . . .	3.4
Nitrogen . . . .	1 do. . . . .	14 . . . . .	11.8
		118	100.

## SECTION IX.

### *Of the Substance of the Brain.*

The medullary matter of the brain and nervous system appears to differ from all other organized substances. It was first examined by M. Thouret, with a view to explain why the brain was exempted from the change, observed in the bodies which were interred in the *Cimetière des Innocens*. Fourcroy after-

wards added many important facts, and corrected M. Thouret in several particulars; and Vauquelin has published an elaborate set of experiments on the same subject. (Thomson's *Annals*, i. 332.)

The medullary substance of the brain is of a soft consistence, and forms, when agitated with water, a sort of emulsion, that passes through the finest sieves. This fluid is coagulated by a temperature of  $160^{\circ}$ , and a quantity of a substance resembling albumen is separated. The same coagulation is produced by acids; but the coagulum differs, in several respects, from that which takes place from the serum of the blood. On being boiled with alcohol, it loses about  $\frac{6}{10}$  of its weight; but one third of the portion, which has been dissolved, is again deposited on cooling, in the form of shining crystalline plates, resembling those which are obtained from biliary calculi, from spermaceti, or from adipocire; but differing from those substances in requiring a higher temperature for its fusion. It stains paper like a fixed oil, is soluble in 20 times its weight of boiling alcohol; and is miscible with water into a sort of emulsion, from which it does not separate on standing, and which is not acid. From the results of its combustion, both alone and with nitre, Vauquelin infers that it contains uncombined phosphorus.

Alcohol, by digesting it with brain, acquires a greenish colour, which it retains even after filtration. By evaporation to one-eighth its bulk, it deposits a yellowish oily fluid, and the liquor itself is yellowish. When repeated quantities of alcohol are digested on the same portion of brain, the alcohol is tinged a sapphire-blue colour. These colours remain, till the whole alcohol is expelled by heat, when the residuary matter acquires a yellow tinge, of greater or less intensity. The latter portions of alcohol do not, like the first, deposit oil on standing.

The liquid oil, after being washed with water, and evaporated to dryness at a gentle heat, has a reddish brown colour, and a smell resembling that of the brain itself, but stronger. Its taste is like that of rancid fat. It forms, with water, an emulsion, which is coagulated by the addition of acids, and by infusion of tan. It is soluble in hot alcohol; and the greater part separates on cooling. Though freed from all acid by washing, yet it furnishes phosphoric acid by being burnt either alone or with nitre; and hence we must admit the presence of phosphorus in this fatty matter, as well as in the crystalline substance. From

the latter, indeed, it appears to differ only in containing a quantity of animal matter, which is separable by cold alcohol.

The alcohol, from which the fatty matter has separated, has a yellow colour, a taste of the juice of meat, and gives marks of acidity. It contains super-phosphate of potassa, and a peculiar animal matter, which, by its solubility in cold alcohol and water; by its property of being precipitated by infusion of galls; by its reddish brown colour, its deliquescence, its taste and smell of the juice of meat, may be regarded as identical with the substance, which Rouelle formerly called saponaceous extract of meat, and to which Thenard has given the name of *osmazome*. It is this substance which tinges the fatty matter, extracted from brain by alcohol. It is found also accompanying muscular fibre or flesh; and has been discovered by M. Morin of Rouen in the root zedoary. (Duncan's Supp. p. 15.)

The portion of brain, which remains after the full action of alcohol, is a greyish white matter in the form of flocks, which resembles cheese externally. In drying, it assumes a grey colour, a semi-transparency, and a fracture similar to that of gum-arabic. It appears, as Fourcroy supposed, to be perfectly identical with albumen; and it is this ingredient which occasions the coagulation of brain, when mixed with water, by heat, acids, metallic salts, &c. The alkaline solution of this part of brain precipitates acetate of lead of a dark brown colour, showing obviously the presence of sulphur.

The medulla of the brain, when exposed to the air, soon undergoes spontaneous decomposition; and evolves an acid, before it passes to the putrid state; but under water it may be kept a long time without any change. Nitric acid does not produce the same effects upon it, as on other animal substances. No nitrogen is separated; but, when the temperature is raised, a large quantity of carbonate of ammonia is disengaged, and oxalic acid is found in the retort.

Diluted sulphuric acid partly dissolves brain, and coagulates another part. The acid solution becomes black when concentrated by evaporation; sulphurous acid is generated; and crystals are formed which consist of sulphate of ammonia. Besides this salt, sulphates of ammonia and lime, phosphoric acid, and phosphates of soda and ammonia are found in the liquid.

When brain is dried at the temperature of boiling water, it coagulates and some water separates from it. When distilled

in close vessels, ammonia is disengaged: which, uniting with carbonic acid, formed at the same time, composes carbonate of ammonia. A portion of oil is obtained also, and sulphureted and carbureted hydrogen gases are formed. In the retort a coal remains which affords traces of phosphates of lime and soda.

The mass of brain, as appears from the experiments of Vauquelin, is composed, therefore, of 1st, two fatty matters, which are probably identical; 2dly, albumen; 3dly, osmazome; 4thly, different salts; and, among others, phosphates of potassa, lime, and magnesia, and a little common salt; 5thly, phosphorus, 6thly, sulphur. The following is to be considered merely as an approximation to their proportions.

1. Water .....	80.00
2. White fatty matter .....	4.53
3. Red fatty matter .....	0.70
4. Albumen .....	7.00
5. Osmazome .....	1.12
6. Phosphorus .....	1.50
7. Acids, salts, sulphur .....	5.15

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100.



## CHAPTER XIV.

## OF CHEMICAL ANALYSIS.

## SECTION I.

*Of the Analysis of Mixed Gases.*

HAVING already, in former parts of this work, enumerated the properties common to the whole class of gaseous bodies, and described the apparatus required for submitting them to experiment, and having also given the chemical history of each individual gas, it would be equally tedious and useless to enter, in this place, into minute details respecting them. Nor could it serve any useful purpose to frame rules for analyzing every possible mixture of gaseous substances; for nearly thirty gases, the number actually known, would give almost endless varieties of combinations, many of which are not at all likely to occur to the analyst. The rules, too, themselves would be unnecessary to those who are qualified to undertake researches into this difficult part of experimental chemistry. All, therefore, that I shall attempt, will be to lay down a few simple directions for discriminating the several gases, and for analyzing such mixtures of them, as are occasionally formed by chemical processes, or are presented to us by nature.

There are two fluids which are used to confine gases for the purpose of examination and analysis, *viz.*, mercury and water. Upon the former, very few gases act sufficiently to interfere with its fitness for retaining them unaltered. Chlorine and nitrous acid gases are the principal exceptions to this remark; for they are both speedily condensed by mercury; and sulphureted hydrogen acts also upon that metal, though not in the same degree. With the exception, however, of nitrous acid gas, those aëriiform substances that cannot be kept over mercury may, in general, be preserved over water, especially if its temperature be raised to 65° or 70° Fahr.; at least they may be kept long enough to enable us to examine their properties, and their proportions in any mixture. For the reception of sulphu-

reted hydrogen and carbonic acid gases, Gaultier de Claubry recommends a cold saturated solution of sulphate of magnesia, as being much less capable of absorbing them than simple water.

The two following Tables exhibit a view of the different gases, and the fluids best adapted for preserving them :

I. *Gases which are best confined by Mercury.*

Oxides.	Combustible.	Acid Gases.
Protoxide of chlorine	Ammonia	Muriatic acid
Peroxide of ditto	Cyanogen	Hydriodic do.
		Sulphurous do.
		Fluoboric do.
		Fluosilicic do.
		Carbonic do.
		Chloro-carbonic do.

II. *Gases confinable by Water.*

Gases that support Combustion.	Combustible Gases.	Incombustible.
Oxygen	Hydrogen	Nitrogen
Chlorine	Carbureted do.	Carbonic acid
Nitrous oxide	Olefiant do.	
——— gas	Phosphureted do.	
	Bi-hydruret of phosphorus	
	Sulphureted do.	
	Tellureted do.	
	Arsenureted do.	
	Selenureted do.	
	Carbonic oxide	

*Examination of Gases confinable by Mercury.*

I. When we have a quantity of any unknown gas standing over mercury, it is desirable first to ascertain in what proportion it is capable of being absorbed by water. For this purpose a small quantity of water, not exceeding 1-80th or 1-100th of the volume of the gas, may be admitted to a portion of it contained in a graduated tube. If the whole gas rapidly disappear, and its place be filled with mercury, it must have consisted of one or more of the following gases:

Ammonia, of which 1 vol. water absorbs	670 vols.
Fluoboric acid .....	700
Fluosilicic .....	260
Hydriodic .....	+ 500
Muriatic .....	480

Sulphurous acid, being soluble only to the extent of about thirty-three times the volume of the water, is not taken up with so much rapidity, or by so small a proportion of water, as the other five gases. Protoxide and peroxide of chlorine are still less absorbable; for of each of these, 1 volume of water condenses only about 8 volumes.

II. To determine whether the gas has acid or alkaline properties, a small slip of litmus paper may be first introduced into it. If it be reddened, the gas must be acid; if not changed, a slip either of litmus paper reddened by vinegar, or of turmeric paper, may be passed up, when the alkaline nature of the gas will be indicated by the usual change of colour to blue or brown. Acid and alkaline gases cannot both exist together in the same mixture, as they immediately condense each other into a solid form.

III. *Ammonia*, when indicated by the colour tests, may either be pure, or may be mixed with cyanogen, or perhaps with one of the oxides of chlorine? (a) If pure, it will entirely disappear by contact with 1-100th its volume of water. (b) If any portion be left unabsorbed, let it be agitated with a little liquid potassa, and if an absorption now take place, pass up a small quantity of solution of per-sulphate of iron with an excess of acid. Cyanogen will be indicated by the blue colour of the liquid. (c) The oxides of chlorine will be distinguished by their greenish yellow colour, by their smell, and by their power of supporting combustion, without exhibiting the characters belonging to oxygen, chlorine, or the oxides of nitrogen.

#### *Acid Gases.*

IV. Of the acid gases, there are four, which, when suffered to escape into the atmosphere, produce a *dense white smoke*, owing to their powerful attraction for aqueous vapour. These are the muriatic, fluoboric, fluosilicic, and hydriodic acids.

V. A property common to all the powerfully acid gases, *viz.*, the fluoboric, fluosilicic, hydriodic, muriatic, and sulphurous, is, that they are absorbed by *fragments of borax*, which salt has

no action on either of the oxides of chlorine, or on carbonic or chloro-carbonic acids.

(a) If the borax, after being thus exposed, be powdered and strongly heated with a little charcoal, and the product be then moistened with water, or with diluted muriatic acid, the presence of *sulphurous acid* will be indicated by a smell of sulphureted hydrogen.

(b) If the gas, which has been absorbed by the borax, be *muriatic acid*, on dissolving the salt in water and adding nitrate of silver, a precipitate will appear, which will be soluble in liquid ammonia, and insoluble in diluted nitric acid. This precipitate, after being well washed, dried, and fused, will, for every 100 grains, indicate 24.5 grains, of chlorine, equivalent to very nearly 25.1 grains, or 64 cubic inches of the acid gas.

VI. A test of the presence of *sulphurous acid*, which acts upon that gas, but not on the other acid gases, is the peroxide of lead. According to Dr. Thomson, it may be employed to absorb sulphurous acid from the other acid gases.

VII. The mixture of acid gases which is likely most frequently to occur, is that of *muriatic* and *sulphurous acids*, or one of them, with *carbonic acid*.

(a) From a measured portion of a mixture of these three gases contained in a graduated tube, the muriatic acid gas will be absorbed by 1-50th its bulk of water.

(b) From another portion of the mixture, contained in a similar tube, peroxide of lead will absorb the sulphurous acid only.

(c) From a third portion, both the muriatic and sulphurous acids will be absorbed by fragments of borax, leaving the carbonic acid separate.

The volume of the three gases, thus determined, ought, if the analysis be correct, to make up a sum total, equal to that of the mixture.

VIII. Hydriodic, hydro-bromic, fluoboric, fluosilicic, and chloro-carbonic acid gases are of such rare occurrence, that it may be sufficient to point out a few tests by which they may be discriminated.

(a) If a little chlorine be passed into a gas containing *hydriodic acid*, a violet-coloured cloud will be immediately produced, the chlorine seizing the hydrogen of the acid gas, and detaching purple vapours of iodine.

(b) When borax has been made to absorb *hydriodic acid gas* free from any admixture of muriatic acid, its solution in water precipitates nitrate of silver; but the precipitated iodide of silver is insoluble in ammonia, and by this property may be separated from chloride of silver.

(c) A slip of white paper introduced into a gas over mercury, betrays the presence of *fluoboric acid gas*, by being immediately blackened.

(d) *Fluosilicic acid gas* is manifested by its producing minute white flakes of silica, in a portion of water which has absorbed any considerable quantity of the gas.

(e) *Chloro-carbonic acid* is decomposed by contact with water; muriatic acid is formed, and remains in solution. Carbonic acid is also produced, equal in volume to the original gas, and may be made apparent, by first saturating the muriatic acid with a little ammonia, and then adding lime water, which will form a white precipitate, consisting of carbonate of lime.

#### *Gases confinable by Water.*

IX. All gases are more or less absorbable by water, but some of them are taken up to a much greater amount, and with much less agitation, than others. It affords, indeed, some insight into the nature of a gas, to ascertain the proportion in which it is capable of being absorbed by water. The water employed for this purpose should have been deprived, as completely as possible, of its air by long boiling; and should have been cooled out of contact with atmospheric air. The best method of applying water is by means of a caoutchouc bottle and tube, resembling that represented plate ii. fig. 21; but the tube, as well as the bottle, should be much larger than are commonly used for eudiometrical purposes.

#### *Water absorbs,*

Twice its vol. of	{	Chlorine gas, Sulphureted hydrogen, Selenureted hydrogen.
An equal vol. of	{	Nitrous oxide, Carbonic acid.
One-eighth its vol. of	{	Olefiant gas, Bi-hydruret of phosphorus.

$\frac{1}{8}$ th to  $\frac{1}{20}$ th its vol. of { Nitrous gas,  
Oxygen gas.

$\frac{1}{7}$ th to  $\frac{1}{40}$ th its vol. of { Phosphureted hydrogen,  
Tellureted hydrogen.

$\frac{1}{30}$ th to  $\frac{1}{4}$ th its vol. of { Nitrogen,  
Hydrogen,  
Carbureted hydrogen,  
Arsenureted hydrogen.

It is necessary, however, to observe that considerable differences in the absorbability of gases are produced by their being pure, or mixed with each other. The information, therefore, which can be thus obtained, is only of a very general kind, and must in no case supersede the application of other methods of analysis.

X. The effects of the watery solution of any gas upon the *colour tests* should next be examined. All the stronger acids, it has already been stated, redden litmus. The same effect is produced, though less readily and distinctly, by cyanogen, carbonic acid, sulphureted hydrogen, and tellureted hydrogen. Chlorine destroys vegetable blues; and the oxides of chlorine first redden litmus, and then destroy its colour. The other gases, which are permanent over water, do not affect vegetable blue colours.

XI. When the quantity of a gas is sufficient to enable us to determine its *specific gravity*, we obtain a datum of great importance for determining its nature. This is best done in the manner already described, vol. i. p. 19. The specific gravity found by experiment may be compared with those of the gases exhibited in the Table, vol. i. p. 149.

XII. Of the gases, which are capable of existing at common temperatures over water, two only are distinguished by being themselves *coloured*. Chlorine is yellowish green, and nitrous acid gas of an orange-red; but the latter is so quickly absorbed by water, that its colour can only be seen when first formed by the mixture of nitrous and oxygen gases.

XIII. The *odour* of gases discriminates several of them. Oxygen, hydrogen, nitrogen, and both the varieties of carbureted hydrogen, if pure, have little or no smell. All the rest have characteristic odours. That of chlorine is peculiar, and very suffocating; that of nitrous gas can only be perceived in a state of mixture with the air already present in the nostrils, with

which it forms nitrous acid. All the other compounds of hydrogen have powerful and generally disagreeable odours.

XIV. The gases, which are *absorbed by liquid potassa*, are cyanogen, chlorine and its oxides, carbonic acid, and sulphureted, tellureted, and selenureted hydrogen. Those acid gases, that are permanent only over mercury, are of course copiously soluble in liquid potassa, but they are not expelled again, like the gases which have been enumerated, unless we add an acid that attracts potassa more strongly than the gas absorbed.

XV. A leading distinction among gases permanent over water, is into such as are capable of *supporting combustion* (that of a wax taper for example) and such as *extinguish flame*. One of the first experiments, then, that should be tried on any unknown gas, is the effect of immersing a lighted taper in it. In oxygen gas, and in nitrous oxide, the taper will burn with great brilliancy; and if blown out, and again plunged into either of those gases, the ignited wick will be rekindled with a slight explosion. The same effect is produced by the two oxides of chlorine. In chlorine, it burns a short time with a dense smoke, and is then extinguished. Nitrous gas does not support the flame of a taper, but sulphur and phosphorus continue to burn when introduced in a state of combustion into that gas.

#### *Gases that support Combustion.*

XVI. *Oxygen gas* may be recognised in any mixture by the action of nitrous gas, which, when mingled with it, produces red fumes of nitrous acid and a diminution of volume. With proper attention to the manner of making the mixture, and to other circumstances described vol. i. p. 337, the proportion of oxygen may be thus determined. Oxygen may also be measured by combustion with hydrogen, and by other processes, which are referred to in the Index, article *Eudiometer*.

XVII. *Chlorine* is discoverable by its yellowish green hue, its suffocating smell, and still more distinctly by its power of discharging vegetable colours.

(a) If chlorine be mingled with other gases which are incapable of being absorbed by liquid potassa, its separation is very simple, and its quantity is determinable by the amount of the absorption produced by that liquid.

(b) Its proportion in more complicated mixtures may be ascertained by admitting, to a measured portion of the gas, an

equal volume of olefiant gas. After standing a quarter of an hour completely excluded from the light, a diminution of volume will be perceived, the amount of which, divided by 2, shows very nearly the quantity of chlorine contained in the mixture.

XVIII. *Nitrous oxide* supports the flame of a candle, and forms with hydrogen gas a detonating mixture; but nitrous oxide is not diminished in volume when mingled with nitrous gas, a property which distinguishes it from oxygen. From chlorine, it differs in being colourless, and almost free from smell, and in being only about half as absorbable by water.

XIX. *Nitrous gas* is diminished in volume, dense red fumes being at the same time produced, when it is mingled with oxygen gas or with atmospheric air. From the amount of its diminution under certain circumstances, its quantity may be estimated. (See vol. i. p. 336.) Nitrous gas is distinguished, also, by the property of being absorbed by the solution of green sulphate of iron, and, by means of that solution, may be separated from several other gases.

XX. *Incompatible gases*.—Of the gases that support combustion, oxygen and nitrous gas cannot exist together in the same mixture, since they mutually condense each other. So also do nitrous gas and chlorine, or its protoxide.

(a) *Chlorine* and *oxygen* gases are separable from each other by liquid potassa, which absorbs the chlorine only. In the same way, chlorine may be separated from nitrous oxide.

(b) *Oxygen* and *nitrous oxide* may be separated by a solution of nitrous gas in sulphate of iron, which condenses the oxygen only.

(c) *Nitrous gas* may be absorbed from a mixture with *nitrous oxide*, by solution of green sulphate of iron, which acts only on the former gas.

#### *Examination of Combustible Gases.*

XXI. *Odour*.—Some insight into the nature of these gases may be gained from their odour. Hydrogen and its compounds with carbon are, when pure, nearly free from odour. Sulphureted hydrogen resembles the washings of a gun-barrel; bi-hydruret of phosphorus has a peculiar odour, difficult to describe, but resembling that of onions; phosphureted hydrogen a similar smell in a still greater degree; arsenureted hydrogen that of garlic; tellureted hydrogen resembles sulphureted



hydrogen; and selenureted hydrogen has a most penetrating smell of horse-radish, and, even in very small quantity, excites a painful inflammation of the membrane of the nostrils.

XXII. *Spontaneous inflammability*.—Phosphureted hydrogen (vol. i. p. 461) is the only gas that takes fire spontaneously, when suffered to escape into the atmosphere.

XXIII. *Action of pure alkaline solutions*.—Sulphureted, tellureted, and selenureted hydrogen are the only species of inflammable gases that are rapidly absorbed by liquid potassa.

XXIV. *Action of chlorine*.—Chlorine acts upon all the combustible gases, but with phenomena peculiar to each.

(a) Both varieties of *phosphureted hydrogen* inflame spontaneously when brought into contact with chlorine, and, if in sufficient quantity, even detonate loudly.

(b) *Sulphureted hydrogen* is immediately decomposed by chlorine, and sulphur is precipitated. One volume of the inflammable gas requires, for complete decomposition, one volume of chlorine.

(c) *Olefiant gas* is speedily condensed by chlorine into an oily-looking liquid, with an ethereal smell, which floats on the surface of the water. One volume of olefiant gas condenses one volume of chlorine. Hence it is easy, by dividing the diminution of volume by 2, to estimate the amount of the former gas. The olefiant gas should be added to the chlorine in a graduated tube shaded from the light, and about a quarter of an hour should be allowed for the full effect to be produced, especially if the tube be of small diameter.

(d) *Hydrogen* and *carbureted hydrogen* are not acted upon by chlorine, provided the mixture be made and preserved in a tube from which all light, both direct and reflected, is carefully excluded. But the ordinary light of day, and still more the direct rays of the sun, falling on the mixture, occasions a speedy action of the gases on each other; and if the quantity be considerable, and the proportions properly adjusted, an explosion often ensues.

XXV. *Action of nitrous gas on inflammable gases*.—(a) Nitrous gas, beside being acted upon by oxygen, by chlorine and its protoxide, and by sulphurous acid gas, is also condensed by *phosphureted hydrogen* and by *sulphureted hydrogen*. When mingled with the last-mentioned gas, the decomposition

is slow, sulphur is deposited, and ammonia and nitrous oxide are formed.

(b) On *hydrogen*, and both the varieties of *carbureted hydrogen*, nitrous gas has no action at common temperatures. It may, therefore, be employed to determine the proportion of oxygen in a mixture of oxygen gas or atmospheric air with any of those three gases, according to the rules given vol. i. p. 337.

XXVI. *Action of the solution of sub-chloride (oxymuriate) of lime.*—This solution, Mr. Dalton finds, absorbs phosphureted hydrogen, converting it into phosphoric acid and water, but has no action on simple hydrogen. It is probably inefficient, also, on the two varieties of carbureted hydrogen, except by remaining some time in contact with them.

XXVII. *Solutions of acetate of lead and nitrate of mercury.*—These solutions, even when heated to 120° Fahrenheit or upwards, absorb sulphureted hydrogen, but do not affect the other combustible gases; nor do they, at that temperature, act on carbonic acid. A similar property belongs also to carbonate of lead precipitated by carbonate of ammonia from a cold solution of the acetate. In all these cases, a copious black precipitate is formed, consisting of the sulphuret of lead or of mercury. The use of carbonate of lead in separating sulphureted hydrogen from other gases, I find to be susceptible of such great precision (Ann. of Phil. xv. 35), that it is capable of detecting one part of sulphureted hydrogen when mixed with 20.000 of any other gas.

Such are the principal agents required in operating on the inflammable gases. By using them in succession, considerable progress may be made towards the analysis of mixtures of these gases. It may be proper to add a few rules for distinguishing the individual gases of this class, and estimating their quantities.

XXVIII. Tellureted, potassureted; selenureted, and arsenureted hydrogen are of such rare occurrence, that it may be sufficient to enable the experimenter to recognise them, if a few of their leading characters are here enumerated.

(a) *Tellureted hydrogen* is absorbed by liquid potassa, but not by acetate of lead. It is decomposed when mixed with chlorine, and if that gas be transmitted through the solution of tellureted hydrogen in liquid potassa, the liquid acquires the

property of forming a white precipitate with alkaline carbonates, and a black one with hydro-sulphurets. (Children's Translation of Thenard, p. 25.)

(b) *Potassureted hydrogen* is instantly decomposed when brought into contact with water; hydrogen is liberated; and potassa formed.

(c) *Arsenureted hydrogen* has a nauseous smell, is sparingly soluble in water, is not absorbed by liquid potassa, but is instantly decomposed by chlorine, and condensed into a liquid, from which water, impregnated with sulphureted hydrogen, throws down a yellow flaky precipitate. When mingled with gases that support combustion, it is discoverable by introducing a lighted taper into a tube filled with the gas, the sides of which will be immediately covered with a chesnut-brown hydruret of arsenic.

(d) *Selenureted hydrogen* may be recognised by its odour (xxi.) by its absorbability by water, with which it affords a solution that in a few minutes becomes opalescent, reddish on the surface, and then deposits selenium. The watery solution reddens litmus, has an hepatic flavour, and gives a permanent brown stain to the skin; but by keeping is entirely decomposed.

XXIX. The mixtures, which may be expected most frequently to occur, of combustible gases with each other, are those of hydrogen, sulphureted hydrogen, carbureted hydrogen, olefiant gas, and carbonic oxide, occasionally with small proportions of nitrogen or carbonic acid gases.

Of these gases, there are three which may be removed from such a mixture by very simple processes, *viz.*, sulphureted hydrogen, carbonic acid, and olefiant gas.

(a) *Sulphureted hydrogen* may be absorbed, as already directed, by solution of acetate of lead, or by carbonate of lead fresh precipitated from the acetate, and diffused through a small quantity of water. Neither of these substances acts on carbonic acid or olefiant gases.

(b) After having thus removed the sulphureted hydrogen, liquid potassa will absorb the *carbonic acid*, and will indicate its quantity by the amount of the absorption.

(c) Or we may act on one portion of the entire gas with potassa, and on another with acetate or carbonate of lead. The latter affecting only the sulphureted hydrogen, we may deduct

the absorption it produces from the total absorption by potassa; and the remainder will show the proportion of carbonic acid. For example, if the absorption by potassa be 10 measures, and by lead 2, then  $10 - 2 = 8$  shows the carbonic acid.

(d) *Olefiant gas* mixed with one or more of the following gases, *viz.*, hydrogen, carbureted hydrogen, carbonic oxide, or nitrogen, may be detected and estimated as follows: Into a graduated tube, about three-tenths of an inch in diameter, pass twenty, twenty-five, or thirty measures of chlorine, observing its quantity when actually in the tube, which is then to be shaded from the light by an opaque cover of tin or pasteboard. To the chlorine pass up fifty measures of the gas under examination; let the mixture stand ten or fifteen minutes; and then gradually raise the cover till the surface of the water within the tube appears. Note the diminution, and divide its amount by 2, which will give the quantity of olefiant gas.

(e) Wash the residuum of the process (d) with liquid potassa. This will absorb any redundant chlorine. The mixture may now contain one or more of the following gases, *viz.*, hydrogen, carbureted hydrogen, carbonic oxide, and nitrogen.

XXX. To analyze exactly mixtures of *hydrogen, carbureted hydrogen, carbonic oxide, and nitrogen*, is a problem of considerable difficulty. If an approximation be all that is wanted, it may be obtained by the following method: Fire a small volume in a Volta's eudiometer over mercury, with 1.5 or 2 vols. of oxygen gas, the degree of whose purity has been previously ascertained, and which must be employed in a proportion somewhat exceeding what is necessary for saturating the inflammable gas. Note the amount of the diminution after firing: then admit liquid potassa to the gas, and observe how much is absorbed; and ascertain the proportions of oxygen and nitrogen in the residue, by processes which will be presently described.

In estimating the composition of a mixed gas, from the phenomena and results of its combustion, the following Table will be found useful. Olefiant gas is included, though not strictly necessary, in order to render the view of these compounds more complete. In each case, it is necessary to employ more oxygen than is strictly required to saturate the inflammable gas; for the combustion will otherwise be imperfect.

*Table showing the Results of Firing the Combustible Gases with Oxygen.*

Names of Gases.	Sp. gr.	100 vols. require oxygen	Total.	Diminished by firing.	Carbonic acid produced.
Olefiant gas . . . .	.9722	300	400	200 = $\frac{1}{2}$	200
Carb. hydrogen . . .	.5555	200	300	200 = $\frac{2}{3}$	100
Hydrogen gas . . . .	.0690	50	150	150 = $\frac{2}{3}$	0
Carbonic oxide . . .	.9722	50	150	50 = $\frac{1}{3}$	100

(a) If the gas under examination afford no carbonic acid by combustion with an excess of oxygen, it may then be either *hydrogen* only, or *hydrogen with a proportion of nitrogen*. In the first case, two measures of the gas will have condensed one of oxygen, making a diminution of three measures. In the second case, the diminution will be less than three measures. It is unnecessary to repeat in this place the directions which have already been given, vol. i. p. 258, for analyzing mixtures of hydrogen and nitrogen gases.

(b) If the gas be found to have condensed twice its volume of oxygen, and to have given an equal volume of carbonic acid, it may be considered as pure *carbureted hydrogen gas*.

(c) If, while it affords an equal volume of carbonic acid, it has consumed only half its volume of oxygen, these are the characters of pure *carbonic oxide*.

(d) But if the gas under examination does not answer exactly in its characters to any one of those enumerated in the table, it may be inferred to be a mixture of two or more of the three last, with perhaps a proportion of nitrogen.

(e) The presence of nitrogen will be indicated by our finding, in the residuary gas after the action of liquid potassa, more nitrogen than can be traced to the oxygen gas employed for effecting the combustion. To decide this, add to the residue nearly twice its volume of hydrogen, and pass an electric spark through the mixture. If an explosion take place, we shall learn the amount of the residuary oxygen by dividing the diminution of volume on firing by 3, and the quotient, deducted from the whole residue, will show its proportion of nitrogen. If the quantity of nitrogen, thus determined, agree with that which formed part of the oxygen gas, no nitrogen is indicated in the

inflammable gas; but if it exceed, the additional quantity must be referred to the combustible gas.

(f) If the mixture consist of hydrogen, carbureted hydrogen, and carbonic oxide, without any nitrogen, the proportions of each may be investigated as follows: Take the specific gravity of the gas in the way already directed, vol. i. p. 19, and then try what hypothetical proportions will most nearly agree with the characters of the mixture. An example will perhaps best explain the method of proceeding.

Let us take, then, the example of a gas of specific gravity 0.7012, 100 vols. of which have been found by experiment to afford by combustion 70 vols. of carbonic acid, the oxygen expended being 110 vols. and the diminution on firing amounting to 140 vols. Now, on inspecting the table, it must be obvious that these 70 vols. of carbonic acid cannot all have been produced from carbureted hydrogen, for in that case they would have required 140 vols. of oxygen, whereas only 110 vols. of oxygen have been spent. Part of the carbonic acid must therefore have resulted from another gas requiring less oxygen than is consumed by carbureted hydrogen; and the only gas answering to this description is carbonic oxide, the presence of which in the mixture may hence be safely inferred. The levity of the mixed gas indicates, also, that it contains hydrogen, which is also rendered probable by the amount of the diminution on firing. On trying various proportions, the following will be found to afford the best explanation of the phenomena and products of combustion:

	Consume oxygen.	Give carbonic acid.	Condensed by firing.
40 vols. of carb. hydrogen ..	80. ....	40. ....	80.
30 — carbonic oxide ..	15. ....	30. ....	15.
30 — hydrogen .....	15. ....	0. ....	45.
100	110.	70.	140.

The specific gravity of such a mixture ought to be

$$.9722 \times 4 = 3.8888$$

$$.690 \times 3 = .2070$$

$$.9722 \times 3 = 2.9166$$

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$$7.0124 \div 10 = 0.70124.$$

Such a coincidence of specific gravity with the results of combustion affords a strong presumption that the proportions

assigned to a gaseous mixture are not very remote from the true ones.

(g) A method of analysis, however, more deserving of confidence, and capable, indeed, of bringing us acquainted with the true constitution of mixtures of these gases, is derived from a set of experiments upon them, which I have described in the *Philosophical Transactions* for 1824.

It has been stated in a former part of this work (vol. i. p. 259), that when platinum in a spongy form is introduced, at common temperatures, into a mixture of hydrogen and oxygen gases in certain proportions, it causes their immediate combination, and the production of water, either silently or with detonation, according to circumstances. The same effect is produced generally, without explosion, by small spherules or pellets made of two parts of fine clay and three of spongy platinum, worked into a paste with water, and then moulded into small balls about the size of peas, which are to be first dried slowly, and then at a stronger heat. By neither of these means, however, is the action of oxygen excited, at common temperatures, on *olefiant gas*, *carbonic oxide*, or *carbureted hydrogen*; but at temperatures between the boiling point of water and that of mercury, those gases also may be made to unite with oxygen in contact with the sponge, and each gas at a different temperature.

*Carbonic oxide*, mixed with oxygen in due proportion, and in contact with the spongy metal, begins to be converted into carbonic acid between 300 and 310° Fahr., and is completely acidified under 340°.

*Olefiant gas* under the same circumstances begins to be acted upon at 480°, and is entirely changed into carbonic acid and water below 520°.

*Carbureted hydrogen* requires a temperature exceeding 550°, and probably not much less than 600°.

These facts suggested to me the possibility of separating hydrogen, carbonic oxide, olefiant gas, and carbureted hydrogen from each other, by exposing a mixture of those gases, with oxygen sufficient to saturate the whole, to contact with spongy platinum at a succession of different temperatures. To simplify the process, however, it is advisable, in the first instance, to remove the olefiant gas by chlorine, in the manner already pointed out, (xxiv. c.) The remainder, after being washed by caustic potassa to separate any excess of chlorine, consists of

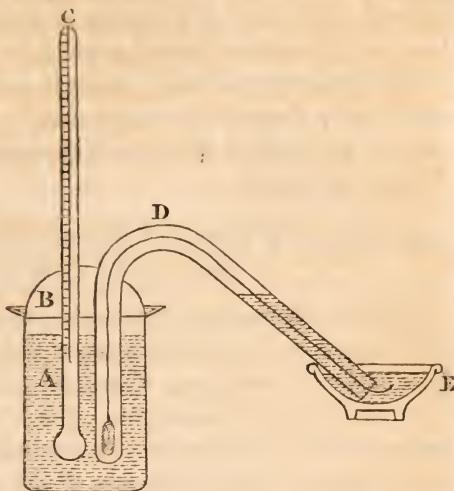
hydrogen, carbonic oxide, and carbureted hydrogen, with or without an admixture of nitrogen gas. In order to learn the quantity of oxygen which it is necessary to add, a previous experiment must be made by firing a small quantity of the gas, which we are about to examine, with excess of oxygen in a Volta's eudiometer; and from the oxygen left we may determine how much has been expended. We can then employ rather more oxygen than the gas which we are about to analyze requires for saturation.

It is a prudent precaution, also, before acting on any quantity of the mixture approaching to a cubic inch, to try the effect of one of the pellets, which, after being fastened to a piece of platinum wire, may be heated red-hot by the blow-pipe, allowed to cool for a minute, and then be introduced through the mercury of the trough to half a cubic inch of the mixture, to which oxygen has been added, confined in a graduated tube. If an immediate action take place, evinced by a rapid diminution of volume and an evident formation of water, and sometimes even by the ignition of the ball, it would be unsafe to introduce the spongy metal into such a mixture, since it would most probably cause detonation. It would be unnecessary, too, because the hydrogen and carbonic oxide only, unless the action of the ball has been such as to excite distinct ignition, will have combined with oxygen, leaving the carbureted hydrogen untouched. The ball may therefore be withdrawn by means of the wire; and the residuary gas allowed to cool to the temperature of the air. The diminution of volume being then noted, the quantity of carbonic acid formed must be determined by liquid potassa; and the oxygen left be ascertained, which, deducted from the original quantity, will show how much oxygen has been expended. Now it is known that every volume of carbonic oxide, to become 1 vol. of carbonic acid, unites with half a volume of oxygen. It is easy, therefore, to calculate how much of the oxygen has been spent in forming water, and, doubling its volume, we have that of the hydrogen gas in the mixture. In this way we arrive at the quantities of hydrogen and carbonic oxide. The proportions of carbureted hydrogen and nitrogen in the residue are easily determined by methods already described.

If no effect be produced, on a portion of gas mixed with oxygen, by introducing one of the platinum balls in the manner directed, we may then pass a piece of the spongy metal itself



into a known volume of the gas over mercury, and if still no action takes place, the analysis will require an increased temperature, which may be applied in the following manner: A sheet-iron vessel (not tinned), A, is to be provided, capable of holding mercury, about 3 inches diameter and  $3\frac{1}{2}$  deep, with a hemispherical cover, B, of the same metal, in which are two holes, the one for the stem of a thermometer, C, graduated up to  $600^{\circ}$  F., the other for the bent tube, D. This tube may be of the



diameter of five-tenths to eight-tenths of an inch, from  $3\frac{1}{2}$  to  $4\frac{1}{2}$  inches long from the sealed extremity to the curved part, and  $7\frac{1}{4}$  or 8 inches from the bend to the open extremity. After mixing a portion of the gas under examination with the due quantity of oxygen, introduce as much of the mixture into the bent tube filled with and inverted in mercury, as will occupy the space shown by the figure, and note the quantity. Then pass up through the mercury a piece of platinum sponge tied to a thin wire of the same metal, which must be left projecting a little out of the open end; and introduce the tube into the mercury contained in the iron vessel, the cover and thermometer being already in their places. The open end of the tube may either be kept in the mercurial trough, or, by stopping it for a time with the finger, it may be placed, as represented in the cut, in a small basin of mercury. The quicksilver in the vessel A must now be heated by an Argand lamp to  $310^{\circ}$  or  $320^{\circ}$ , and kept at a temperature not exceeding the latter during ten or fifteen minutes. The first effect of the heat is to expand the volume of gas, but presently a diminution ensues, and, after a still further interval, water is evidently formed. When the action of the gases on each other ceases, as indicated by the level of the mercury within the tube remaining stationary, the tube may be removed, and allowed to cool. The residuary

volume must be accurately measured, and the quantities of carbonic acid formed and oxygen expended ascertained as already directed, from which data may be deduced the proportion of carbonic oxide and of hydrogen in the original gas. The carbureted hydrogen and nitrogen are to be determined as before.

In this way considerable quantities of gas may be operated upon, and a degree of precision may be attained much beyond what is practicable when small quantities only are fired in a Volta's eudiometer.

*Analysis of Mixtures of Inflammable Gases, with Gases that support Combustion.*

XXXI. No mixture, it must be obvious, can exist of gases that support combustion with gases that are spontaneously inflammable; for instance, of oxygen, nitrous oxide, or chlorine with phosphureted hydrogen. Nor is sulphureted hydrogen compatible with chlorine or with nitrous gas; nor chlorine with olefiant gas, or indeed with any of the varieties of carbureted hydrogen, unless light be carefully excluded from the mixture. But oxygen gas and atmospheric air may be, and the latter frequently is, mingled with hydrogen, carbureted hydrogen, olefiant gas, or carbonic oxide.

(a) A mixture of hydrogen and oxygen gases may be examined either by exploding the mixture (rendering it combustible, if not already so, by adding more hydrogen), or by the action of nitrous gas, or of a solution of nitrous gas in sulphate of iron.

(b) Atmospheric air mixed with hydrogen may be investigated by two separate experiments, the one for determining oxygen, the other nitrogen, by rules already given, vol. i. p. 258.

(c) The presence of oxygen gas in olefiant gas, carbureted hydrogen, or carbonic oxide, may be easily ascertained by the effect of adding nitrous gas, which produces a dense red vapour and a diminution of volume; and the quantity of oxygen may be estimated in the manner described vol. i. p. 337. For detecting nitrogen, and ascertaining its quantity, rules have already been given, XXX. d.

*Mixtures of Condensable Vapours with Gases.*

XXXII. There are several vapours which, at ordinary temperatures, are capable of existing as such, in a state of mixture

with atmospherical air and other gases. In this state, it does not appear that the vapour is united with the gas by any affinity, but rather that, according to the theory of Mr. Dalton, it has a distinct and independent existence; for each vapour, when mingled with air or any other gas, at a certain temperature, has exactly the same tension or elasticity, which it would have *in vacuo* at the same temperature. (See vol. i. page 125.) It is easy, then, by inspecting the tables contained in the Appendix to this work, showing the force of the vapours of various fluids at different temperatures, to ascertain what proportion those vapours form of the whole weight of any gas. For example, at 60° Fahr. and 30 inches of the barometer, atmospheric air, fully charged with moisture, contains aqueous vapour, the force of which is equivalent to one-fiftieth that of the whole atmosphere. In vol. i. p. 24, rules are given for calculating what proportion of any mixture of gas and vapour the vapour constitutes, at a given temperature and pressure. With respect to the vapour of water, this is a correction which requires frequently to be made in calculating the weight of gases; and the same formula, which enables us to determine it in that case, is applicable to others, if for 0.620 (the specific gravity of steam), we substitute the specific gravity of any other gas or vapour, that may be the subject of investigation.

The vapours which may be occasionally mixed with permanent gases are,

(a) *Aqueous vapour, or the steam of water.*—This must necessarily exist in all gases confined by water, and its quantity will be proportionate to the temperature, as shown in the table of the force of vapour. The proportion which it constitutes of any gas, at a given temperature, may be determined by the rules given vol. i. p. 24.

Gases, standing over mercury, frequently also contain aqueous vapour. Its presence may be shown, either by surrounding with a freezing mixture a portion of the gas contained in a glass tube, when the inner surface of the tube will be obscured by a thin film of ice; or it may be discovered by a few bubbles of fluoboric gas, which occasion a dense white cloud. From gases confined over mercury, aqueous vapour may be removed, by bringing into contact with them chloride of calcium, recently cooled from a state of fusion.

(b) *Nitrous acid vapour.*—This is sufficiently distinguishable

by its red colour, and its odour of nitrous acid. It is incompatible with sulphureted, phosphureted, tellureted, or arsenureted hydrogen, with ammonia, with sulphurous acid when water is present, and probably with hydriodic acid.

(c) *The vapour of alcohol* may be known by its odour, but it does not, at common temperatures, form a combustible mixture with atmospheric air or oxygen gas.

(d) *The vapour of ether* composes with oxygen gas an inflammable mixture which detonates violently.

All the three foregoing vapours are separated from permanent gases by passing the mixture through water, but ether less readily than others.

(e) *The vapour of naphtha* is distinguishable by its peculiar smell. At common temperatures it does not form a combustible mixture with oxygen. It has so little affinity for water, that a gas, with which it is mingled, may be several times passed through water, and even kept over that fluid without being deprived of it. (Saussure, Ann. of Phil. x. 120.)

(f) *The vapour of sulphuret of carbon* may be known by its smell, and by the other properties belonging to that substance, described vol. i. p. 492.

There are various other substances which yield vapours capable of forming permanent mixtures with the gases; but they are not likely to become subjects of examination, and in general they are present only in small quantity, and are sufficiently discriminated by the characters of smell and colour. Such are the vapours of iodine and bromine.

### TABLE,

*Referring to the Methods of detecting the different Gases, and analyzing Mixtures of them with each other.*

N. B. The numerals, unless otherwise expressed, refer to the foregoing paragraphs.

*Air, atmospheric.* (See the Index to this work, article Eudiometer.) Mixed with combustible gases, XXXI.

*Ammonia.* Absorption by water, I. Separation from other gases, III.

*Bi-carbureted hydrogen.* See *hydrogen, bi-carbureted.*

*Bi-hydroguret of phosphorus.* See *hydrogen, phosphureted.*

*Borac.* Gases absorbed by, V.

*Carbonic acid.* Separation from muriatic and sulphurous acid gases, VII. From sulphureted hydrogen, &c. XXIX. a, b, c.

*Carbonic oxide.* Characters, and method of estimating its quantity, XXX. c.

*Carbureted hydrogen.* See *hydrogen, carbureted.*

*Chlorine.* Tests of, XVII. a. Separation from other gases, b. From oxygen gas, XX. a. Action on combustible gases, XXIV.

*Chlorine, protoxide of, I.* Characters, III. c.

———— peroxide of, I. Characters, III. c.

*Chloro-carbonic acid, VIII. e.*

*Colours of gases, III. c. XII.*

*Combustible gases, XXI.* Mixtures with supporters of combustion, XXXI.

*Combustion, gases that support, XV. XVI. &c.*

*Cyanogen.* Tests of, III. b.

*Fluoboric acid gas.* Absorption by water, I. Tests of, VIII. c.

*Fluosilicic acid gas.* Absorption by water, I. Tests of, VIII. d.

*Gases, acid, II. IV.* Fuming, IV.

———— absorption by water, IX.

———— alkaline, II.

———— coloured, XII.

———— combustible, XXI. XXX.

———— that support combustion, XV. XVI.

———— incompatible, II. XX. XXXI. XXXII. b.

———— odour of, XIII. XXI.

*Gravity, specific, of gases, XI.* Its coincidence with analytic results, XXX. e.

*Hydriodic acid gas.* Absorption, I. Tests of, VIII. a, b.

*Hydrogen gas.* Characters, XXX. a. How estimated when mixed with other combustible gases, XXX.

*Hydrogen, arsenureted.* Odour, XXI. Characters, XXVIII. c.

*Hydrogen, bi-carbureted. (Olefiant gas.)* Action of chlorine, XXIV. c. Separation from other gases, XXIX. d.

*Hydrogen, bi-hydroguret of, XXIV. a.*

*Hydrogen carbureted.* Action of chlorine, XXIV. *d.* How separated from other gases, XXX. Characters, XXX. *b.*

*Hydrogen, phosphureted,* XXIV. *a.*

————— *potassureted.* Tests of, XXVIII. *b.*

————— *selenureted.* Odour, XXI. Characters, XXVIII. *d.*

*Hydrogen, sulphureted.* Odour, XXI. Action of chlorine, XXIV. *b.* Absorbed by hot solutions of lead and mercury, XXVII. XXIX. *a.*

*Hydrogen, tellureted.* Odour, XXI. Characters, XXVIII. *a.*

*Litmus.* Gases that redden it, X.

*Muriatic acid gas.* Absorption by water, I. By borax, V. *b.* Analysis of mixtures of, VII.

*Nitrogen, with oxygen gas.* (*See air, atmospheric.*) Analysis of mixtures of, with combustible gases, XXX. *d.*

*Nitrous acid vapour,* XXXII. *b.*

*Nitrous gas.* Tests of, XIX. Action on combustible gases, XXV. Separation from oxygen gas, XX. *c.*

*Nitrous oxide.* Tests of, XVIII. Separation from oxygen gas, XX. *b.*

*Odour of gases.* XIII. XXI.

*Olefiant gas.* See *Hydrogen, bi-carbureted.*

*Oxygen gas.* Tests of, XVI. Separation from chlorine, XX. *a.*; from nitrous oxide, XX. *b.*; from nitrous gas, XX. *c.*; from combustible gases, XXV. *c.*; XXXI. *d.*

*Phosgene.* See *Chloro-carbonic acid gas.*

*Phosphureted hydrogen.* See *hydrogen.*

*Potassa, liquid,* gases absorbable by, XIV. XXIII.

*Sulphureted hydrogen.* See *hydrogen, sulphureted.*

*Sulphurous acid.* Absorption by water, I.; by borax, V. *a.*; by peroxide of lead, VI. Separation from muriatic acid gas, VII. *b.*; from carbonic acid, VII. *c.*

*Tellureted hydrogen.* See *hydrogen tellureted.*

*Vapours mixed with gases,* XXXII.

*Water.* Action on gases, I. IX. Steam of, in gases, XXXII. *a.*

## SECTION II.

*Directions for examining Mineral Waters.*

The complete and accurate analysis of mineral waters, and of mineral bodies in general, is one of the most difficult subjects of chemical manipulation, and requires also a very extensive acquaintance with the properties and habitudes of a numerous class of substances. Long and attentive study of the science is therefore essential, to qualify any one for undertaking exact and minute determinations of the proportions of the component parts of bodies. Such minuteness, however, is scarcely ever required in researches that are subservient to the ordinary purposes of life; a general knowledge of the composition of bodies being sufficient to assist in directing the most useful applications of them; and this, generally speaking, may be obtained by experiments that require, for their performance, only a moderate share of skill in practical chemistry. In some instances, however, where a variety of foreign substances are present in a natural water, it requires extensive chemical knowledge and great consideration, to devise the proper experiments, and to draw the proper inferences from their results. Much, indeed, must always be left to the judgment of the operator, and this will be materially assisted by a careful study of the best models of this kind of investigation, which are to be found in the analyses of particular waters by Black, Lavoisier, Marcet, Phillips, Gay Lussac, and several other eminent chemists.

Before proceeding to the analysis of a mineral water, it is proper to inquire into its natural history, and to examine attentively its physical characters. The nature of the strata in the neighbourhood of the spring will often furnish useful suggestions respecting the contents of the water; the period of the year should be stated at which the analysis was performed; and whether after a rainy or dry season. The temperature of the water must be carefully observed, as it issues from the spring; and the quantity inquired into which it yields in a given time. The sensible qualities of taste, smell, degree of transparency, &c., are also best ascertained at the fountain head. The specific gravity of the water may be found by weighing a bottle, which is capable of containing a known weight of distilled water at a certain temperature, filled with the water under examination

at the same temperature; or by the use of a very sensible hydrometer, as recommended by Mr. Dalton. (Manchester Society's Memoirs, N. S. iii. 54.) It is proper, also, to examine, on the spot, the channel through which the water has flowed; to collect any deposit that may have been formed; and to investigate its nature.

The effects of heat on the water may be next tried.—Many waters lose their transparency when their temperature is raised, and let fall a considerable deposit. The quality of this may, in some degree, be conjectured from its appearance. If its colour be brownish yellow, it consists, either wholly or chiefly, of oxide of iron; if white, or nearly white, it is composed principally of the carbonate of lime or of magnesia, or of both carbonates. A mineral water, containing iron, deposits the oxide of that metal also, when exposed to the atmosphere; and a thin yellowish pellicle forms on its surface, whether stagnant in a natural reservoir, or collected in a separate vessel. By this exposure, iron may be sometimes discovered in a water, though not easily detected at first; in consequence of its becoming farther oxidized, and more sensible to the action of tests. An exception, however, to this remark will be stated in describing the application of the test of tincture of galls. Sulphureted waters deposit a sediment, even when preserved in a well-closed phial; the hydrogen quitting the sulphur, which settles in the form of a white powder, combustible when dried.

#### ART. I.—*Examination of Mineral Waters by Reagents.*

Water is never presented by nature in a state of complete purity. Even when collected as it descends in the form of rain, chemical tests detect in it a minute proportion of foreign ingredients. And when it has been absorbed by the earth, has traversed its different strata, and is returned to us by springs, it is found to have acquired various impregnations. The readiest method of judging of the contents of natural waters, is by applying what are termed *tests*, or *reagents*; *i. e.* substances which, on being added to a water, exhibit, by the phenomena they produce, the nature of the saline, or other ingredients.—For example, if on adding infusion of litmus to any water, its colour is changed to red, we infer, that the water contains an uncombined acid: if this change ensue, even after the water has been boiled, we judge that the acid is a fixed, and not a



volatile one : and if, on adding the muriate of baryta, a precipitate falls down, we safely conclude that the peculiar acid, present in the water, is either entirely, or in part, the sulphuric acid. I shall first enumerate the tests generally employed in examining waters, and describe their application ; and, afterwards, point out by what particular tests the substances, generally found in waters may be discovered.

In many instances, a mineral water may contain a saline, or other ingredient, but in such small quantity as to escape the action of tests. It is therefore advisable to apply the tests of fixed substances to the water, after reducing its bulk one half, or in some cases considerably more, by evaporation, as well as in its natural state.

The use of tests, or reagents, has been employed by Mr. Kirwan to ascertain, by a careful examination of the precipitate, not only the *kind*, but the *quantity*, of the ingredients of mineral waters. This will be best understood from an example. It is an established fact, that 100 parts of crystallized chloride of sodium, when completely decomposed by nitrate of silver, yield, as nearly as possible, 240 of precipitated chloride of silver. From the weight of the precipitate, separated by nitrate of silver from a given quantity of any water, it is therefore easy, when no other muriatic salt is present, to infer, what quantity of chloride of sodium was contained in the water ; since every hundred grains of fused chloride of silver indicate, pretty accurately,  $41\frac{1}{2}$  of crystallized common salt. The same mode of estimation may be applied in various other instances ; and the rule for each individual case will be stated in the following description of the use of the various reagents. The scale of equivalents will give, by mere inspection, the quantities of different salts, from which the precipitates that are obtained have resulted. It is, indeed, an instrument quite essential in prosecuting investigations of this kind.\*

For the analysis of mineral waters, and of mineral bodies in general, tests of the utmost purity are required. These will be found enumerated in their order in the following pages, and they are all absolutely necessary in investigating the composition of natural waters. It will be found extremely useful to keep the three mineral acids, the alkalis, and the alkaline car-

\* See the directions for its use, prefixed to the Table of Equivalents in the Appendix at the end of this volume.

bonates, in a liquid form, and of such strength, that one measure of the one will neutralize either one measure, or some simple multiple of one, of the other. The advantage thus obtained is, that when it is necessary to precipitate a substance, held in solution by an acid, we can take just the quantity of alkali required for the purpose; a precaution of great use in all cases where the substance to be precipitated is redissolved by adding an excess of the precipitant; as happens, for instance, with respect to alumina, which is precipitated by the proper quantity of potassa, and redissolved by adding more. It is of no consequence of what precise strength these solutions are; but the following will be found of convenient density; and, though I am well aware that the numbers require a little correction in some instances, yet they are sufficiently accurate for the purpose they are intended to serve.

Liquids.	Sp. gravity.	Measures for saturation.	100 Water gr. measure contain.
Sulphuric acid . . . .	1.134	1	15.7 gr. real
Nitric acid . . . . .	1.142	1	23.27 gr. do.
Muriatic acid . . . .	1.074	1	11.89 gr. do.
Potassa . . . . .	1.100	2	9.3 gr. do.
Soda . . . . .	1.070	2	6.1 gr. do.
Ammonia . . . . .	0.970	1	
Subcarb. potassa ..	1.248	1	31. gr. dry
——— soda . . . .	1.110	2	11.5 gr. dry
——— ammonia	1.046	2	

The first column of the foregoing Table expresses the specific gravity of the liquid test; the second, the number of measures of each required for saturating any of the others; and the third, the number of grains of real acid, real alkali; or solid carbonate, in 100 measures of solution, each measure being equal to a grain of water. From the last column, with the aid of the *Scale of equivalents*, it is easy to calculate how much of any other test, of known composition, is required for decomposing 100 water grain measures of any of the solutions in the table. Thus, 15.7 grains of real sulphuric acid will be found, by Dr. Wollaston's scale, to be capable of decomposing 41.2 grains of dry chloride of barium (equal to 48 of the crystallized salt). It may be advisable, therefore, to keep muriate of baryta, of such strength, that 400 water grain measures may be equivalent to 48 grains of the crystals; in which state the solution will be more convenient for use, than if it

were stronger. The same plan may be extended to other tests, the quantities of which may thus be accurately adjusted to the purpose intended to be answered. Indeed, it would contribute very much to accuracy, as well as to economy, if all the chemical solutions, kept for purposes of research, had their specific gravity, and the proportion of their ingredient in a real or solid state, marked on the labels of the bottles containing them,—a practice of which I have long experienced the advantages. When we are thus provided with tests of known purity and strength, Mr. Dalton recommends that we drop, into a measured quantity of the water under examination, certain known quantities of each test from a dropping tube graduated into grains, till the required effect is produced; then from the quantity of the test expended, the quantity of saline matter in the water may be determined without the trouble of collecting the precipitate; or if the latter be done, the one method will be a check upon the other. (Manchester Society's Memoirs, N. S. iii. 61.)

When filters of paper are used for collecting precipitates, great caution is necessary that their weight should be the same, before and after the experiment. Even during the time of weighing, they acquire moisture from the atmosphere; and it is therefore necessary, before taking their weight correctly, to obtain an approximation to it; after which, the paper being again dried, less time is occupied in determining its weight within the minute fraction of a grain. The unsized paper, which accompanies Mr. Watt's copying machines, answers the purpose extremely well. This sort was always employed by Berzelius, whenever he used filters at all; but their use, when the nature of the precipitate admits, he thinks should be avoided. (78 Ann. de Chim. 31.) Another source of fallacy pointed out by Dr. Thomson (First Princ. ii. 294) is sulphate of lime, which was discovered in all the filtering paper he could procure; and this, in certain cases, may introduce errors into analysis, if no allowance be made for it. I am not inclined, however, to coincide in the total rejection of filters, and am of opinion that, when they are carefully and skilfully used, there is no better way of collecting and drying precipitates. In order to wash away, completely, all soluble matter, a stream of distilled water should be directed upon the edge of the paper, when laid in the funnel, either from a dropping tube or from the bottle, fig. 25, *a*.

I.—*Infusion of Litmus, Syrup of Violets, &c.*

The infusion of litmus is prepared by steeping, for several hours, that substance, first bruised in a mortar, and tied up in a linen bag, in distilled water, which extracts its blue colour. If the colour of the infusion tend too much to purple, it may be amended by a drop or two of solution of pure ammonia; but of this no more must be added than is barely sufficient, lest the delicacy of the test should be impaired. It is apt to lose its colour in closely stopped bottles, but regains it by the admission of air. (Liebig.)

The syrup of violets is not easily obtained pure. The genuine syrup may be distinguished from the spurious by a solution of corrosive sublimate, which changes the former to green, while it reddens the latter. When it can be procured genuine, syrup of violets is an excellent test of acids, and may be employed in the same manner as the infusion of litmus. It indicates, also, the presence of alkalis, which turn it green.

Paper stained with the juice of the March violet, or with that of the scrapings of radishes, answers a similar purpose; being turned red by acids, and green by alkalis. In staining paper for the purpose of a test, the paper must be used unsized; or, if sized, it must previously be well washed with warm water; because the alum, which enters into the composition of the size, changes vegetable blue colours to red.

In the *Philosophical Magazine*, vol. i. page 180, may be found some recipes for other test liquors, invented by the late celebrated Mr. Watt.

Infusion of litmus is a test of most uncombined acids.

1. If the infusion redden the unboiled, but not the boiled water, under examination; or if the red colour, occasioned by adding the infusion to a recent water, return to blue, on boiling; we may infer, that the acid is a volatile one, and most probably the carbonic acid. Sulphureted hydrogen gas, dissolved in water, also reddens litmus, only before boiling; but its presence is easily recognized by its offensive smell.

2. To ascertain whether the change be produced by carbonic acid or by sulphureted hydrogen, when experiment shows that the reddening cause is volatile, add a little lime-water, or, in preference, barytic water. This, if carbonic acid be present, will occasion a white precipitate, which will dissolve, with effervescence, on adding a little muriatic acid. Sulphureted hydro-

gen may also be contained, along with carbonic acid, in the same water; which will be determined by the tests hereafter to be described.

In some cases, when the change of colour in the litmus solution is so slight as to be scarcely perceptible, it may be proper to use half a pint or more of the water which we are examining, and to mix it with the infusion of litmus in a broad shallow glass vessel, set on a sheet of white paper; using for the sake of comparison a similar vessel of distilled water, coloured by an equal quantity of the litmus infusion.

3. Paper tinged with litmus is also reddened by the presence of carbonic acid, but regains its blue colour on drying. The mineral and fixed acids redden it permanently. That these acids, however, may produce their effect, it is necessary that they should be present in a sufficient proportion. (See Kirwan on Mineral Waters, p. 40.) The dark blue paper, which is generally wrapped round loaves of refined sugar, is not discoloured by carbonic acid or sulphureted hydrogen, but only by the stronger acids.

II.—*Infusion of Litmus reddened by Vinegar,—Spirituous Tincture of Brazil-wood,—Tincture of Turmeric, and Paper stained with each of those three Substances,—Acid Tincture of Cabbage,—Syrup of Violets.*

All these different tests have one and the same object.

1. Infusion of litmus reddened by vinegar, or litmus paper reddened by vinegar, has its blue colour restored by pure alkalis and pure earths, and by carbonated alkalis and earths. This effect is even produced by carbonate of lime dissolved by a considerable excess of carbonic acid; for in this case the fixed acid, which reddens the litmus, is neutralized by the lime, and the volatile carbonic acid is displaced. Hence it is that lime, though supersaturated with carbonic acid, acts like an alkali on vegetable colours.

2. Turmeric paper and tincture are changed to a reddish brown by alkalis, whether pure or carbonated, and by pure earths, but not by carbonated earths. Dr. Bostock finds that it is obviously affected by a solution, containing only  $\frac{1}{2000}$  of its weight of potassa.

Turmeric paper, it must however be stated, is turned brown by muriatic acid gas and by strong acids in general; by boracic

acid; by sub-acetate of lead; by all the soluble salts of iron except the acetate; by submuriate of zinc; and by several other metallic salts, which are enumerated by Mr. Faraday. (Quarterly Journal, xiii. 315.)

3. The red infusion of Brazil-wood, and paper stained with it, become blue by alkalis and earths, and even by the latter when dissolved by an excess of carbonic acid. In the last-mentioned case, however, the change will either cease to appear, or will be much less remarkable, when the water has been boiled. It has been shown also, by Bonsdorff, that both the paper and tincture are affected by acids, a rose colour being generally produced, but in a manner and degree varying with each particular acid. (Annals of Phil. N. S. iv. 23.)

4. Infusion of the leaves of red cabbage in very dilute sulphuric acid (*viz.* two or three drops to a pint of water) has a red colour, which is rendered blue by alkalis, provided they be added in quantity just sufficient to neutralize the acid. Hence, if the infusion be made with a known quantity of acid, it becomes a test of the quantity of alkali in any solution. As it is apt to spoil by keeping, it should be prepared fresh when wanted, from the leaves, which have been dried carefully, and preserved in corked vials.

5. Syrup of violets, when pure, is, by the same agents, turned green; as is also paper stained with the juice of the violet, or with the scrapings of radishes.

In preference to the syrup, Mr. Descroizilles recommends as a test the *pickle* of violets, prepared by adding common salt to the expressed juice. (Annales de Chimie, lxvii. 80; or Nicholson's Journal, xxv. 232.) The colour tests already enumerated are, I believe, sufficient for every purpose. Various others, however, have been recommended; juice of elderberries, in Ann. of Phil. viii. 384; alcoholic extract of cabbage, viii. 304; alkanet, v. 395; the petals of the Iris, Quart. Journ. xv. 161.

### III.—*Tincture of Galls.*

Tincture of galls is the test generally employed for discovering iron; with all the combinations of which it produces a deep blue or black tinge, more or less intense, according to the quantity of iron. The iron, however, which, in natural waters, exists in the state of protoxide, in order to be detected by this test, must be peroxidized. If oxidized in a less degree, its

effect will not be apparent, unless after standing some time in contact with the air, or adding some substance, such as a little of the solution of chloride of lime, which speedily converts the protoxide into peroxide. By applying tincture of galls before and after evaporation or boiling, we may know whether the iron be held in solution by carbonic acid, or by a fixed acid: for,

1. If it produce its effect before the application of heat, and not afterward, carbonic acid is the solvent.

2. If after boiling and filtration through paper, as well as before, a mineral acid is the solvent.

3. If, by the boiling, a yellowish powder be precipitated, and yet galls continue to strike the water black, the iron, as often happens, is dissolved both by carbonic acid and by a fixed acid. A neat mode of applying the gall-test was used by M. Klaproth, in his analysis of the Carlsbad water; a slice of the gall-nut was suspended by a silken thread in a large bottle of the recent water, and so small was the quantity of iron, that it could only be discovered in water fresh from the spring, by a slowly-formed and dark cloud surrounding the re-agent. (Klaproth, vol. i. page 279.)

It has been remarked by Mr. R. Phillips, that the presence of carbonate of lime modifies considerably the action of the gall test on iron. When the iron is at the minimum of oxidation, it rather heightens the colour produced by this test; but when the metal is in the state of peroxide, it diminishes the effect so much, that a very minute quantity of iron may elude entirely the action of the gall test. An ounce measure of solution of carbonate of lime, containing  $\frac{1}{8000}$ th of a grain of protoxide of iron, was sensibly affected by tincture of galls: but the same proportion of protoxide, by being converted into peroxide, ceased any longer to affect the test. (See Children's Translation of Thenard, p. 250.)

Another circumstance, which interferes with the action of tincture of galls as a test of iron, is the presence of various organic matters, whether animal or vegetable. Thus Rose has remarked that serum of blood, added to a solution of peroxidized iron, protects that metal from the agency of galls and other tests.

#### IV.—*Sulphuric Acid.*

1. Sulphuric acid discovers, by a slight effervescence, the

presence of carbonic acid, whether uncombined or united with alkalis or earths.

2. If lime be present, whether pure or uncombined, the addition of sulphuric acid occasions, after a few days, a white precipitate of sulphate of lime. If from a mineral water, which has been well boiled, the addition of sulphuric acid extricates sulphureted hydrogen gas, Mr. Westrumb infers the presence of hydrosulphuret of lime. In this case, also, sulphate of lime is precipitated. (Nicholson's Journal, xviii. 40.)

3. Baryta is precipitated by sulphuric acid instantly, in the form of a white powder.

4. Nitric and muriatic salts, in a dry state, or dissolved in very little water, on adding sulphuric acid, and applying heat, are decomposed; and if a stopper, moistened with solution of pure ammonia, be held over the vessel, white clouds will appear. For distinguishing whether nitric or muriatic acid be the cause of this appearance, rules will be given hereafter.

5. Sulphuric acid is, also, a delicate test of the presence of vegetable or animal matter. When to any water, containing organic matter, sulphuric acid is added, and the water is evaporated, it acquires a distinct brown colour, which becomes deeper as the liquor becomes more concentrated, and is not removed by filtration.

#### V.—*Nitric and Nitrous Acids.*

These acids, if they occasion effervescence, give the same indications as the sulphuric. The fuming red nitrous acid has been recommended as a test distinguishing between hepatic waters that contain hydro-sulphuret of potassa, and those that contain merely sulphureted hydrogen gas. In the former case, a precipitate ensues on adding nitrous acid, and a very fetid smell arises; in the latter, a slight cloudiness only appears, and the smell of the water becomes less disagreeable. If a water, after boiling, gives a precipitate of sulphur, on adding nitrous acid, Westrumb concludes that this is owing to hydro-sulphuret of lime.

The presence of nitric acid in a mineral water may be discovered by applying a solution of indigo in sulphuric acid, in the manner pointed out by Liebig, and described vol. i. p. 352.



VI.—*Oxalic Acid and the Alkaline Oxalates.*

The oxalic acid is a most delicate test of lime, which it separates from most of its combinations.

1. If a water, which is precipitated by oxalic acid, become milky on adding a watery solution of carbonic acid, or by blowing air through it from the lungs, by means of a quill or glass tube, we may infer that pure lime (or baryta, which has never yet been found pure in water) is present.

2. If the oxalic acid occasion a precipitate before, but not after boiling, the lime is dissolved by an excess of carbonic acid. In this case, by heating the water, carbonate of lime is separated, in the form of a white sediment, or of a sediment tinged yellow by oxide of iron, when that metal is also present.

3. If oxalic acid occasion a precipitate even after boiling, the solvent of the lime is a fixed acid. A considerable excess of any of the mineral acids, however, prevents the oxalic acid from throwing down a precipitate, even though lime be present; because some acids decompose the oxalic, and others, dissolving the oxalate of lime, prevent it from appearing. (See Kirwan on Waters, p. 88.)

The oxalate of ammonia, or of potassa (which may easily be formed by saturating the respective carbonates of these alkalis with a solution of oxalic acid), are not liable to the above objection, and are preferable as re-agents, especially the latter, to the uncombined oxalic acid. Yet even these oxalates fail to detect lime when supersaturated with muriatic or nitric acids; and, if such an excess be present, it must be neutralized, before adding the test, with pure ammonia. A precipitation will then be produced. The presence of other earths in solution, along with lime, also impedes decomposition by oxalic acid and the oxalates. Thus a watery solution of sulphate of magnesia and sulphate of lime is not precipitated by these tests. This observation, which I had made many years ago, and noticed in former editions of this work, has been verified and investigated by Mr. Walcker. He finds that, by reducing the proportion of a calcareous salt to a magnesian salt held in the same solution, the precipitation by oxalates is rendered much slower and less distinct, and, in quantity, falls much short of that which ought to take place. (Quart. Journ. N. S. iii. 375.)

The quantity of lime, contained in the precipitated oxalate, may be known by first calcining it with excess of air, which

converts the oxalate into a carbonate; and, by expelling from this last its carbonic acid, by calcination, with a strong heat, in a covered crucible, we obtain the pure lime. According to Dr. Marcet, 117 grains of sulphate of lime give 100 of oxalate of lime, dried at  $160^{\circ}$ ; but, as there must always be some uncertainty as to the completeness of desiccation, it is the most accurate method to convert the oxalate into pure lime by calcination. The use of oxalate of ammonia, the same excellent analyst observed, is in some degree limited by its property of precipitating the salts of iron.

The fluuate of ammonia, recommended by Scheele, I find to be a most delicate test of lime. It may be prepared by adding carbonate of ammonia to diluted hydro-fluoric acid, in a leaden vessel, observing that there be a small excess of acid.

#### VII.—*Pure Alkalis and Carbonated Alkalis.*

1. The pure fixed alkalis precipitate most of the earths and all the metals, whether dissolved by volatile or fixed menstrua, but only in certain states of dilution; for example, sulphate of alumina may be present in water, in the proportion of four grains to 500, without being discovered by pure fixed alkalis; and if too much of the alkali be added to a more concentrated solution, the alumina is re-dissolved. If the alkali be perfectly free from carbonic acid, it does not precipitate lime, strontia, or baryta, except when those earths are held in solution by carbonic acid in excess, and then in the state of carbonates.

As the alkalis precipitate so many substances, it is evident that they cannot afford any very precise information, when employed as re-agents. From the colour of the precipitate, as it approaches to a pure white, or recedes from it, an experienced eye will judge that the precipitated earth contains less or more of metallic admixture. Its precise composition must be ascertained by rules which will presently be given.

2. Pure fixed alkalis also decompose all salts with basis of ammonia, which becomes evident by its smell, unless the salts are dissolved in much water, and also by the white fumes it exhibits when a stopper, moistened with muriatic acid, is brought near.

3. Carbonates of potassa and of soda have similar effects.

4. Liquid ammonia precipitates most of the earthy and all the metallic salts; but if quite free from carbonic acid, it does

not precipitate lime, baryta, or strontia, when those earths are held in solution by any acid, except the carbonic; nor does it discover very small quantities of magnesia. It has this advantage as a precipitant of alumina, that when added in excess it does not re-dissolve that earth. To any liquid that contains copper or nickel in a state of solution, ammonia imparts a deep blue colour; the precipitated oxides of those metals being re-dissolved by an excess of the volatile alkali.

5. Carbonate of ammonia has the same properties, except that it does not precipitate magnesia from its solutions at common temperatures. Hence, to ascertain whether this earth be present in any solution, add the carbonate of ammonia till no farther precipitation ensues; filter the liquor; raise it nearly to  $212^{\circ}$  Fahrenheit; and then add pure ammonia. If any precipitation now occurs, we may infer the presence of magnesia. It must be acknowledged that zirconia, yttria, and glucina, would escape discovery by this process; but they have never yet been found in mineral waters; and their presence can scarcely be expected. Of the presence of magnesia another test is described in Section XIX.

#### VIII.—*Lime-Water.*

1. Lime-water is applied to the purposes of a test, chiefly for detecting carbonic acid. Let any liquor, supposed to contain this acid, be mixed with an equal bulk of lime-water. If carbonic acid be present, either free or combined, a precipitate will immediately appear, which, on adding a few drops of muriatic acid, will again be dissolved with effervescence.

2. When lime-water is added to a water containing carbonate of lime dissolved by an excess of carbonic acid, that excess unites with the newly added lime, and forms an insoluble precipitate. In this case, in addition to the carbonate of lime which before existed in the water, a fresh portion of carbonate is formed, and both are precipitated together.

3. When neither uncombined carbonic acid, alkaline or earthy carbonates, alumina, nor oxide of iron, exist in a mineral water, lime-water is one of the best precipitants of magnesia. It is necessary, however, in order to obtain the magnesia, to concentrate the water by evaporation. Less than the twelfth part of a grain of magnesia in a wine pint of water, Mr. Phillips

finds, may be shown to exist by adding lime-water. (Ann. of Phil. N. S. i. 309.)

4. Lime-water will also show the presence of corrosive sublimate by a brick-dust coloured sediment; but of this substance, hydriodate of zinc is a much more sensible test. (See ch. ix. sect. 15.) If arsenious acid (common arsenic) be contained in a liquid, lime-water, when added, will occasion a precipitate, consisting of lime and arsenious acid, which is very difficultly soluble in water. This precipitate, when mixed up with oil, and laid on hot coals, yields the well-known garlic smell of arsenic.

### IX.—*Pure Baryta, and its Solution in Water.*

1. A solution of pure baryta is even more effectual than lime-water in detecting the presence of carbonic acid, and is much more portable and convenient; since, from the crystals of this earth, the barytic solution may at any time be immediately prepared. In discovering carbonic acid, the solution of baryta is used similarly to lime-water, and, if this acid be present, gives, in like manner, a precipitate soluble with effervescence in dilute muriatic acid. This part of the operation may be performed at the spring-head, where we may add sufficient barytic water to precipitate all the carbonic acid; but as sulphates also will be decomposed by the same test, it will be necessary to ascertain the proportions of sulphate and carbonate, by the action of weak muriatic or nitric acid, which will dissolve the carbonate only. It may then be precipitated a second time by carbonate of soda. If the precipitate be dried, and exposed for a very short time to a low red heat, every 100 grains will indicate 22 grains =  $47\frac{1}{2}$  cubic inches of carbonic acid gas.

2. The barytic solution is also a most sensible test of sulphuric acid and its combinations, which it indicates by a precipitate not soluble in muriatic acid.—Pure strontia has similar effects as a test. The quantity of the precipitated substance, indicated by the weight of the precipitate, will be stated in No. XV.

### X.—*Metals.*

1. Of the metals, *silver* and *mercury* are tests of the presence of hydro-sulphurets, and of sulphureted hydrogen gas. If a little quicksilver be put into a bottle containing water impreg-

nated with either of those substances, its surface soon acquires a black film, and, on shaking the bottle, a blackish powder separates from it. Silver is speedily tarnished by the same cause.

2. A beautiful application of *gold leaf* as a test of the presence of small quantities of salts containing nitric acid, has been contrived by Dr. Wollaston. Let the water, suspected to contain any nitrate, be concentrated by evaporation; then add a little sulphuric acid to the heated water, with a small quantity of muriate of soda, unless the water already contain some muriate, when the last-mentioned addition is unnecessary. Immerse a little gold leaf in the mixture, and boil it. If any nitrate be present, the gold leaf will be immediately dissolved, and a smell of aqua regia will generally be perceived. (Dr. Marcet on Sea Water, Phil. Trans. 1822, p. 452; and Faraday in Quart. Journ. xvii. 179.)

3. The metals may be used also as tests of each other, on the principle of elective affinity. Thus, for example, a polished iron plate, immersed in a solution of sulphate of copper, soon acquires a coating of the latter metal; a plate of copper precipitates silver from its solutions; and so on.

### XI.—*Sulphate of Iron.*

When used for the purpose of a test, sulphate of iron has been chiefly employed for ascertaining the presence of oxygen gas, of which a natural water may contain a small quantity.

A water, suspected to contain oxygen gas, may be mixed with a little recently-dissolved sulphate of iron, and kept closely corked up, in a phial completely filled by the mixture. If a yellowish powder be precipitated in the course of a few days, the water may be inferred to contain oxygen gas.

### XII.—*Sulphate, Nitrate, and Acetate of Silver.*

These solutions are all in some measure applicable to similar purposes.

1. They are peculiarly adapted to the discovery of chlorine and muriatic acid, and of chlorides and muriates. The silver, quitting its solvent, combines with the chlorine; and the oxygen, abandoned by the silver, unites with the hydrogen of the muriatic acid. A flaky precipitate of chloride of silver falls down, which, at first, is white, but on exposure to the sun's light acquires a bluish, and finally a black colour. This precipitate,

washed with water acidulated with nitric acid, dried and fused by a gentle heat, Dr. Black states to contain, in 1000 parts, as much muriatic acid as would form  $425\frac{1}{2}$  parts of crystallized common salt, which estimate scarcely differs at all from that of Klaproth. The same quantity of chloride of silver (1000 parts) indicates, according to Kirwan,  $454\frac{3}{4}$  parts of muriate of potassa (chloride of potassium). Dr. Marcet's experiments and my own indicate rather more than 240 grains from 100 of common salt. But in all cases where there is a difference of testimony as to the quantities of any substance indicated by the weight of a precipitate, reference may be had to the Table of Equivalents in the Appendix. This will show that 146 parts of chloride of silver are equivalent to 60 of chloride of sodium, and to 76 of chloride of potassium. Hence 100 grains of fused chloride of silver denote 41 of chloride of sodium, and 52.05 of chloride of potassium. A precipitation, however, may arise from other causes beside the presence of chlorine, which it is proper to state.

2. The solutions of silver in acids are precipitated by carbonated alkalis and earths. The agency of the alkalis and earths may, however, be prevented, by previously saturating them with a few drops of the same acid in which the oxide of silver is dissolved.

3. The nitrate and acetate of silver are decomposed by the sulphuric and sulphurous acids; but this may be prevented by adding previously a few drops of nitrate or acetate of baryta, and, after allowing the precipitate to subside, the clear liquor may be decanted, and the solution of silver added. Should a precipitation now take place, the presence of muriatic acid, or some one of its combinations, may be inferred. To remove uncertainty, whether a precipitation be owing to sulphuric or muriatic acid, a solution of sulphate of silver may be employed in the first instance, which, when no uncombined alkali or earth is present, denotes with certainty the presence of the muriatic acid. According to Professor Pfaff, one part of muriatic acid of the specific gravity 1.15, diluted with 70,000 parts of water, barely exhibits a slight opaline tinge, when tested with nitrate of silver; and, when diluted with 80,000 parts of water, it is not affected at all. Mr. Meyer of Stettin assigns, however, a much more extensive power to nitrate of silver, as a test of muriatic acid.

4. When solutions of silver are added to compounds of chlorine with oxides, for example to chloride of lime (a compound of chlorine with oxide of calcium), no escape of oxygen gas takes place, although the silver cannot unite with chlorine without abandoning its oxygen. This oxygen, detached from the silver, must necessarily unite with the chlorine, and form chloric acid, which constitutes with silver a soluble compound. It is necessary, then, after adding nitrate of silver to solution of chloride of lime till no farther precipitate ensues, to decant the clear liquid, to evaporate it to dryness, and to heat the residuum. Oxygen gas will be disengaged, and to the residuum water acidulated with nitric acid may be added, which will leave the chloride of silver. This process is always necessary when the base of any chloride, which we wish to decompose by nitrate of silver, is a metallic oxide, and not a metal. (Ann. de Chim. et Phys. xi. 108.)

5. The solutions of silver are precipitated by sulphureted hydrogen, and by hydro-sulphurets; but the precipitate is then reddish, or brown or black; or it may be, at first, white, and afterwards become speedily brown or black. It is soluble, in great part, in dilute nitric acid, which is not the case if occasioned by muriatic or sulphuric acid.

6. The solutions of silver are precipitated by vegetable extractive matter; but, in this case, also, the precipitate has a dark colour, and is soluble in nitrous acid.

### XIII.—*Nitrate and Acetate of Lead.*

1. Acetate of lead, the most eligible of these two tests, is precipitated by sulphuric and muriatic acids; but, as we have much better indicators of both these acids, I do not enlarge on its application to that purpose.

2. The acetate of lead is also a test of sulphureted hydrogen, and of hydro-sulphurets of alkalis, which occasion a black precipitate; and, if white paper, on which characters are traced with a solution of acetate of lead, be held over a portion of water containing sulphureted hydrogen gas, they are soon rendered visible; especially when the water is a little warmed.

3. The acetate of lead is employed in the discovery of uncombined boracic acid, a very rare ingredient of waters. To ascertain whether this be present, some cautions are necessary. (a) The uncombined alkalis and earths (if any be indicated by

the colour tests I. and II.) must be saturated with acetic or acetous acid. (b) The sulphates must be decomposed by acetate or nitrate of baryta, and the muriates by acetate or nitrate of silver. The filtered liquor, if boracic acid be contained in it, will continue to give a precipitate, which is soluble in nitric acid of the specific gravity 1.3.

4. Acetate of lead is said, also, by Pfaff, to be a very delicate test of carbonic acid; and that it renders milky water, which contains the smallest possible quantity of that acid. In this case, the precipitate, which is produced, must necessarily be re-dissolved with effervescence, on adding a few drops of acetic or diluted nitric acid.

#### XIV.—*Nitrate of Mercury prepared with and without Heat.*

This solution, differently prepared, is sometimes employed as a test.

1. The solution of nitrate of mercury, prepared without heat (proto-nitrate) has been found by Pfaff to be a much more sensible test of muriatic acid than nitrate of silver. Its sensibility, indeed, is so great, that one part of muriatic acid, of the specific gravity 1.150, diluted with 300,000 parts of water, is indicated by a slightly dull tint ensuing on the addition of the test.

2. It is, at the same time, the most sensible test of ammonia, one part of which, with 30,000 parts of water, is indicated by a slight blackish-yellow tint, on adding the nitrate of mercury. (Saussure, jun.)

3. The nitrate of mercury is also precipitated by highly diluted phosphoric acid; but the precipitate is soluble in an excess of phosphoric or nitric acid, which is not the case if it has been occasioned by muriatic acid.

#### XV.—*Muriate, Nitrate, and Acetate of Baryta.*

1. These solutions are all most delicate tests of sulphuric acid and of its combinations, with which they give a white precipitate, insoluble in diluted muriatic acid. The delicacy of the test is such, that 1 grain of sulphate of soda (containing 0.2469 grain of sulphuric acid) dissolved in 12,000 grains of pure water, is sensibly precipitated by muriate of baryta. (Thomson.) Barytic salts are decomposed, also, by alkaline carbonates; but the precipitate thus occasioned is soluble in diluted muriatic or nitric acid, with effervescence, and may even be prevented, by



adding, previously, a few drops of the same acid, as that contained in the barytic salt which is employed.

One hundred and eighteen grains of dry sulphate of baryta contain very nearly 40 of real sulphuric acid, and are equivalent to about 72 grains of sulphate of soda, and to 68 grains of sulphate of lime, both supposed anhydrous. By these proportions, (subject to correction, for reasons stated vol. i. page 629,) it is easy to calculate, from the actual weight of the desiccated precipitate, what quantity of either of those two salts has been decomposed. From the Table of Equivalents, data may also be obtained for calculating what quantity of any other sulphate is indicated by a known weight of sulphate of baryta. When more than one sulphate is present in any solution, the problem becomes more complex, and requires an acquaintance with the rules for separating the alkaline and earthy bases from each other.

It has been remarked by Berzelius, that when sulphuric acid is precipitated from some of the weaker bases by a barytic salt, the precipitated sulphate of baryta is combined with a portion of those bases. Thus when sulphate of iron or copper is decomposed by muriate of baryta, the sulphate of baryta, after being dried and calcined, is accompanied by oxide of iron or of copper, and assumes a reddish colour in the first case, or a yellowish green in the second. In order, therefore, to determine with precision the quantity of sulphuric acid, it is necessary to remove the precipitated oxide by some acid in which it is soluble. (*Ann. de Chim. et de Phys.* xiv. 376.)

2. By the cautious addition of acetate of baryta, as long as it occasions any precipitate, all the sulphates existing in any solution are decomposed, and their bases are obtained united with acetic acid. By evaporating the liquid to dryness, and calcining the residuum, with free access of air, the acetic acid is destroyed, and the bases of these salts may be obtained separate, or combined only with carbonic acid, and in this state may be recognised by properties more characteristic than those belonging to them in a state of more energetic combination. In this way the alkaline bases may be obtained separately from the earthy ones; for the mere addition of water to the incinerated mass takes up the former, and leaves the latter. For the separation of the alkalis, and of the earths, from each other, rules will be given in the 3d section of this chapter.

3. Phosphoric salts occasion a precipitate, also, with barytic solutions; but the phosphate of baryta is soluble in dilute muriatic and nitric acids without effervescence.

XVI.—*Triple Prussiate, or Ferro-Cyanate of Potassa and of Lime.*

Of these two, the ferro-cyanate of potassa is the most eligible. When pure, it does not speedily assume a blue colour on the addition of an acid, nor does it *immediately* precipitate muriate of baryta. Ferro-cyanate of ammonia is preferred by some chemists, (see Quart. Journ. ix. 408.) but I believe it has no real advantage over that of potassa.

Ferro-cyanate of potassa is a very sensible test of iron, with the solution of which it produces a prussian blue precipitate, in consequence of a double elective affinity. To render its effect more certain, however, it may be proper to add, previously, to any water suspected to contain iron, a little muriatic acid, with a view to the saturation of the uncombined alkalis or earths, which, if present, prevent the detection of very minute quantities of that metal by the prussian test.

1. If a water, after boiling and filtration through paper, does not afford a blue precipitate, on the addition of prussiate of potassa, the solvent of the iron may be inferred to be a volatile one, and probably the carbonic acid.

2. Should the precipitation ensue in the boiled water, the solvent is a fixed acid, the nature of which must be ascertained by other tests.

Doubts had been thrown, by several chemical writers, on the fitness of the ferro-cyanate of potassa for determining the *quantity* of iron in solutions of that metal. But Mr. Porrett, in his able inquiry into the nature of the triple prussiates, has shown that, with certain precautions, the ferro-cyanate of potassa is fully adequate to this purpose. (Phil. Trans. 1814, p. 538.) It is necessary to observe,

1st. That if the ferro-cyanate itself, after being dissolved in water, gives immediately a blue precipitate by the addition of muriatic acid, it is not pure, and will afford a fallacious result.

2dly. That if the salt, however pure, be added *in excess*, to a solution of iron *containing an excess of acid*, and then heated, the prussian blue thrown down will weigh more than it ought; because some is furnished by the decomposition of the

ferro-cyanic acid, contained in that part of the acid, which has been added in excess.

3dly. That prussian blue, even after it has been formed, is materially acted upon by a mixture of nitric and muriatic acids, and, in some degree, by the muriatic acid alone at a boiling heat.

4thly. That prussian blue, when precipitated, always carries with it sulphate of potassa, derived from the liquid from which it is thrown down; and that this sulphate adheres to it so obstinately, that several washings with water, acidulated with sulphuric acid, are necessary to detach it.

5thly. That if the solution, to which the test is applied, contain not only iron, but alumina, oxide of copper, or any other substance, which the test is known to precipitate, *that* substance should be removed, by the usual means, previously to the application of the test.

Suppose then, for example, that we have baryta, alumina, magnesia, and oxides of iron and copper, in a state of solution by nitro-muriatic acid. The solution, if not already neutral, should first be rendered so by the cautious addition of ammonia. The barytic salt may next be decomposed by a solution of sulphate of soda, poured in till it ceases to occasion a precipitate. Ammonia, added to the residuary liquor, throws down the other earths and oxides, and an excess of it will re-dissolve the oxide of copper. From the insoluble part, consisting of alumina, magnesia, and oxide of iron, solution of pure potassa will remove the alumina. The oxide of iron and the magnesia may then be re-dissolved in any suitable acid; and into the solution, neutralized, or nearly so, by ammonia, if necessary, the ferro-cyanate may be poured, till it ceases to produce any effect, taking care to add as little excess as possible. The precipitate washed, dried at a steam heat, and weighed, will indicate in every 100 grains, 34.235 grains of peroxide of iron.

Besides iron, the prussiated alkalis also precipitate muriate of alumina. No conclusion, therefore, can be deduced, respecting the non-existence of muriate of alumina, from any process, in which the prussic test has previously been used. It will, therefore, be proper, if a salt of alumina be indicated by other tests, to examine the precipitate effected by ferro-cyanate of potassa. This may be done by repeatedly boiling it to dryness with muriatic acid, which takes up the alumina, and leaves the prus-

siate of iron. From the muriatic solution, the alumina may be precipitated by a solution of carbonate of potassa.

According to Klaproth (ii. 55), solutions of yttria (which earth, however, is not likely to be present in any mineral water) afford, with the prussian test, a white precipitate, passing to pearl-grey, which consists of prussiate of yttria. This precipitate disappears on adding an acid, and hence may be separated from prussiated iron. The same accurate chemist states, that the prussian test has no action on salts with base of glucina (ii. 55); but that it precipitates zirconia from its solutions (ii. 214.)

The prussiated alkalis decompose, also, all metallic solutions excepting those of gold, platinum, iridium, rhodium, osmium, and antimony.

#### XVII.—*Succinate of Soda and of Ammonia.*

1. The succinate of soda was first recommended by Gehlen, and afterwards employed by Klaproth (Contributions, ii. 48), for the discovery and separation of iron. The salt with base of ammonia has also been used for a similar purpose by Dr. Marcet, late physician to Guy's Hospital, in a skilful analysis of the Brighton chalybeate, which was published in the new edition of Dr. Saunders's Treatise on Mineral Waters.

The succinic test is prepared by slightly super-saturating carbonate of soda or ammonia with succinic acid. Much excess of acid is injurious, by dissolving the succinate of iron. In applying the test, it is necessary not to use more than is sufficient for the purpose; because an excess of it re-dissolves the precipitate. The best mode of proceeding is to heat the solution containing iron, and to add gradually the solution of the succinate, until it ceases to produce any turbidness. A pale red precipitate is obtained, consisting of per-succinate of iron. This, when calcined with a little wax, in a low red heat, gives an oxide of iron, of which 100 parts contain about 70 of the metal, agreeing, therefore, with the peroxide.

2. The succinates, it is stated by Dr. Marcet and Mr. Ekeberg, precipitate alumina also, provided there be no considerable excess of acid in the aluminous salt. On magnesia it has no action, and hence may be successfully employed in the separation of those two earths. If 100 parts of octohedral crystals of alum be entirely decomposed by succinate of ammonia, they give precisely 12 parts of alumina calcined in a dull red heat.

The succinate of ammonia, according to Mr. Ekeberg, (Journ. des Mines, No. lxx.) precipitates glucina; and the same test, according to Klaproth (ii. 214), throws down zirconia from its solutions.

To separate all the iron and alumina from any water, long boiling with free access of air is necessary, in order that the iron may be completely oxidized; or this end will be attained more expeditiously by adding nitric acid, then digesting, and afterwards neutralizing, as exactly as possible, the redundant acid with ammonia, before adding the succinate. On salts with base of the protoxide of iron, the succinates have no action.

#### XVIII.—*Benzoic Acid, and Benzoate of Ammonia.*

Benzoic acid, or, still better, benzoate of ammonia, precipitates iron readily and entirely; and being much cheaper, and more readily obtained, than succinate of ammonia, may be substituted for the latter salt. It has also one advantage over the succinate, *viz.*, that it does not decompose the salts of manganese. (Thomson's Ann. ix. 163; Phil. Mag. xl. 258.)

#### XIX.—*Phosphate of Soda.*

1. A method of completely precipitating magnesia from its solutions has been suggested by Dr. Wollaston. It is founded on the property which fully neutralized carbonate of ammonia possesses; first to cause the solution of the carbonate of magnesia, formed when the ammoniacal carbonate is added to the solution of a magnesian salt, and afterwards to yield that earth to phosphoric acid, with which and ammonia it forms a triple salt. For this purpose, a solution of carbonate of ammonia, prepared with a portion of that salt which has been exposed, spread on a paper for a few hours to the air, is to be added to the solution of the magnesian salt sufficiently concentrated; or to a water suspected to contain magnesia, after being very much reduced by evaporation. No precipitate will appear till a solution of phosphate of soda is added, when an abundant one will fall down.

A neat and effectual way of applying this test was practised by its inventor, as follows:—Spread upon a piece of glass the clear solution supposed to contain magnesia, then add a few drops of the solutions of carbonate of ammonia and phosphate of soda in succession; and trace the word *magnesia*, or any other, upon

the glass so covered, with the end of a glass rod. If magnesia be present, the word which is traced will appear in white characters; if not, no such appearance will result. (Quart. Journ. xiv. 229, xv. 336.)

When the *quantity* of magnesia is to be ascertained, let the precipitate be washed, collected on a filter, and dried in a temperature not exceeding 100° Fahrenheit. One hundred grains of it will indicate 19 of pure magnesia; 44 carbonate; about 66 of muriate of magnesia; and 62 of desiccated, or double that quantity of crystallized, sulphate of magnesia. If, instead of drying the precipitate at a gentle heat, which leaves an uncertain quantity of water in it, we calcine it, we may then reckon the anhydrous phosphate of magnesia to indicate in every hundred grains 41.6 (according to Stromeyer 37) grains of magnesia, equivalent to 124 grains of the anhydrous sulphate of that earth.

Mr. Richard Phillips has suggested (Ann. of Phil. N. S. i. 308) that some fallacy in the use of this test may be occasioned by the carbonate of lime, which all sesqui-carbonate of ammonia contains. Hence the addition of phosphate of soda may throw down phosphate of lime as well as the ammoniaco-magnesian phosphate.

2. Phosphate of soda is also a test of *lithia*, which earth was thus discovered by Berzelius in the mineral waters of Bohemia. Into the mineral water pour a solution of phosphate of soda, evaporate to dryness, and redissolve all that is soluble by cold water. Lithia, if present, is left in the state of an insoluble phosphate of lithia and soda. (Ann. of Phil. N. S. xi. 669.)

## XX.—*Muriate of Lime.*—*Chloride of Platinum.*—*Chloride of Gold.*

1. Muriate of lime is principally of use in discovering the presence of alkaline carbonates, which, though they very rarely occur, have sometimes been found in mineral waters. Carbonate of potassa exists in the waters of Aix-la-Chapelle; that of soda, in the water of Vichy; in some springs in Yorkshire; and in a few other springs and lakes. Carbonate of ammonia was detected by Mr. Cavendish in the waters of Rathbone-place, London. Of all the three carbonates, muriate of lime is a sufficient indicator; for those salts separate from it a carbonate of lime, soluble with effervescence in muriatic acid. If the solution be filtered and evaporated, and the dry residuum be heated, muriate of ammonia

will be known by its volatility. The resulting salts with base of potassa and soda will, under the same circumstances, remain fixed.

2. With respect to the discrimination of the different alkalis, potassa and its compounds may, according to Dr. Wollaston, be detected by the chloride of platinum, which distinctly and immediately precipitates potassa, and is not affected by soda. (See also Faraday in *Quart. Journ.* xvii. 179.) Carbonate of ammonia may be discovered by its smell; and by its precipitating a neutral salt of alumina, while it has no action apparently on cold solutions of magnesian salts.

3. Chloride of gold has been recommended as a most delicate test of protoxide of iron, surpassing even the gall-nut; but it requires the presence of a little carbonate of soda, which, in some cases, may interfere with its use. A precipitate is formed, which gradually assumes a purple colour. (*Quart. Journ.* xv. 382.)

#### XXI.—*Solution of Soap in Alcohol.*

This solution may be employed to ascertain the comparative hardness of waters. With distilled water it may be mixed, without any change ensuing; but, if added to a hard water, it produces a milkiness, and even a curdy appearance, more considerable as the water is less pure. From the degree of this change, an experienced eye will derive a tolerable indication of the quality of the water. This effect is owing to the alkali quitting the oil, whenever there is present in a water any substance, for which the alkali has a stronger affinity than it has for oil. Thus all uncombined acids, and all salts with earthy and metallic bases, decompose soap, and occasion that property in waters which is termed hardness. At the same time an insoluble soap is formed by the union of the oil with the earthy base.

#### XXII.—*Alcohol.*

Alcohol, when mixed in any water, in the proportion of about an equal bulk, precipitates all the salts which it is incapable of dissolving. (See Kirwan on Waters, page 263.)

#### XXIII.—*Hydro-Sulphuret of Ammonia.*

This and other hydro-sulphurets, as well as water saturated with sulphureted hydrogen, may be employed in detecting copper, lead, and arsenic; with the two former of which they give a black, and with the latter a yellowish precipitate.

As those metals, however, are never found in natural waters, I shall reserve, for another occasion, what I have to say of the application of their appropriate tests.

#### XXIV.—*Starch.*

Starch is the appropriate test of iodine, which has been discovered in some brine springs on the Continent; the waters of Sales in Piedmont; (Ann. de Ch. et de Ph. xxiii. 419); in water from a spring at Leith (12 Ann. Phil. 390); and in several of the springs on the Andes,—in one 10,000 feet above the level of the sea. (Quart. Journ. N. S. iii. 384.) If the iodine be combined with a base, it will be necessary to add previously a little muriatic acid. After this,  $\frac{1}{45,000}$ th of iodine is manifested by a violet or purple colour. Nitrate or acetate of silver is a still more delicate test, and may be employed even when common salt is present, because chloride of silver is soluble in ammonia, which the iodide is not. (Quart. Journ. loc. cit.)

#### TABLE,

*Showing the Substances that may be expected in Mineral Waters, and the Means of detecting them.*

*Acids in general.* Infusion of litmus. Syrup of violets, I.

*Acid, boracic.* Acetate of lead, XIII. 3.

*Acid, carbonic.* Infusion of litmus, I. 1, 2. Lime-water, VIII. 1. Barytic water, IX. 1. Acetate of lead, XIII. 4.

*Acid, muriatic.* Nitrate and acetate of silver, XII. Nitrate of mercury, XIV.

*Acid, nitric.* Sulphuric acid, IV. 4. Gold leaf, X. 2. See also vol. i. p. 352.

*Acid, phosphoric.* Solutions of baryta, XV. 2. Nitrate of mercury, XIV. 3.

*Acid, sulphurous.* By its smell,—and destroying the colour of litmus, and of infusion of red roses;—by the cessation of the smell a few hours after the addition of the black oxide of manganese.

*Acid, sulphuric.* Solution of pure baryta, IX. Barytic salts, XV. Acetate of lead, XII.

*Albumen.* Discovered hitherto only in the water of Vichy. (See Quart. Journ. xli. 180.)

*Alkalis in general.* Vegetable colours, II. Muriate of lime, XX.

*Alumina dissolved by acids.* Succinates XVII.



*Ammonia*, by its smell and tests, II. Nitrate of mercury, XIV. 2.

*Baryta and its compounds*, by sulphuric acid, IV.

*Bromine*. By the successive action of chlorine and sulphuric ether, on the water previously reduced to one-eighth or one-tenth of its bulk by evaporation. (See vol. i. p. 246.)

*Carbonates in general*. Effervesce on adding acids, without any unpleasant smell.

*Earths dissolved by carbonic acid*. By a precipitation on boiling;—by pure alkalis, VII. Solution of soap, XXI.

*Hydriodates*. Starch, XXIV.

*Hydro-sulphuret of lime*. Sulphuric acid, IV. Nitrous acid, V.

*Iodine*. Starch, XXIV.

*Iron dissolved by carbonic acid*. Tincture of galls, III. 1. Ferro-cyanate of potassa, XVI. 1. Succinate of ammonia, XVII. Benzoate of ammonia, XVIII.

*Iron dissolved by sulphuric acid*. Same tests, III. 3. XVI. 2. XVII.

*Lime in a pure state*. Water saturated with carbonic acid. Blowing air from the lungs. Oxalic acid, VI.

*Lime dissolved by carbonic acid*. Precipitation on boiling. Caustic alkalis, VII. Oxalic acid, VI.

*Lime dissolved by sulphuric acid*. Oxalate of ammonia, VI. Barytic solutions, IX. and XV.

*Lithia*. Phosphate of soda, XIX. 2.

*Magnesia dissolved by carbonic acid*. Precipitation on boiling,—the precipitate soluble in dilute sulphuric acid.

*Magnesia dissolved by other acids*. Precipitated by pure ammonia, not by the carbonate, VII. 5. Phosphate of soda, XIX. Lime-water, VIII. 3.

*Muriates of alkalis*. Solutions of silver, XII.

——— of lime. Solutions of silver, XII. Oxalic acid and oxalate of ammonia, VI.

*Nitrate of potassa, and other nitrates*. Gold leaf, X. 2.

*Oxygen gas*. Sulphate of iron, XI.

*Potassa, and its salts*. Chloride of platinum, XX. 2.

*Silica*. A precipitate by muriate of ammonia not soluble in dilute nitric acid.

*Soda, carbonate of*. Muriate of lime, XX. 1.

*Sulphates in general*. Barytic solutions, IX. and XV. Acetate of lead, XIII.

*Sulphate of alumina.* Barytic solutions, IX. and XV. A precipitate by carbonate of ammonia not soluble in acetic acid, but soluble in pure fixed alkalis by boiling. Succinates, XVII. 2.

*Sulphate of lime.* Barytic solutions, IX. and XV. Oxalic acid and oxalates, VI. A precipitate by alkalis not soluble in dilute sulphuric acid.

*Sulphate of magnesia.* Barytic solutions, IX. and XV. Phosphate of soda and carbonate of ammonia, XIX.

*Sulphate of potassa.* Barytic solutions, IX. and XV. Muriate of platinum, XX. 2.

*Sulphate of soda.* Barytic salts, IX. and XV. Muriate of platinum, XX.

*Sulphurets of alkalis.* Polished metals, X. Smell on adding sulphuric or muriatic acid. Nitrous acid, V.

*Sulphureted hydrogen gas.* By its smell. Infusion of litmus, I. Polished metals, X. Acetate of lead, XIII. 2.\*

*Vegetable matter.* Sulphuric acid, IV.

#### ART. 2.—*Analysis of Waters by Evaporation.*

Before proceeding to the evaporation of any natural water, its gaseous contents must be collected. This may be done by filling with the water a large glass globe or bottle, capable of holding about 50 cubical inches, and furnished with a ground stopper and bent tube. The bottle is to be placed up to its neck in a tin kettle filled with a saturated solution of common salt, which must be kept boiling for an hour or two, renewing, by fresh portions of hot water, what is lost by evaporation. The disengaged gas is to be conveyed, by the bent tube, into a graduated jar, filled with, and inverted in, mercury, where its bulk is to be determined. On the first impression of the heat, however, the water will itself be expanded, and portions will continue to escape into the graduated jar, till the water has attained its maximum of temperature. This portion must be measured, and its quantity be deducted from that of the water submitted to experiment. If a considerable proportion of gas be contained in a mineral water, the best way of receiving it is into a small gazometer.

\* The vapour of putrefying animal or vegetable matter dissolved in water, according to Klaproth, (see his Contributions, vol. i. p. 590,) often gives a deceptive indication of sulphureted hydrogen.

In determining, with precision, the quantity of gas, it is necessary to attend to the state of atmospheric pressure and temperature, and to other circumstances already enumerated, vol. i. page 22, where rules for reducing observations made under different states of the barometer and thermometer, to a mean standard, will be found.

The gases, most commonly discovered in mineral waters, are *carbonic acid*; *sulphureted hydrogen*; *nitrogen gas*; *oxygen gas*; and, in the neighbourhood of volcanoes only, *sulphurous acid gas*. To determine the proportion of these and other gases, constituting a mixture obtained from any mineral water, full directions have already been given in the first section of this chapter.

The vessels employed for EVAPORATION should be of such materials as are not likely to be acted on by the contents of the water. I prefer those of unglazed biscuit ware, made by Messrs. Wedgwood; but, as their surface is not perfectly smooth, and the dry mass may adhere so strongly as not to be easily scraped off, the water, when reduced to about one-tenth of its volume, or less, may be transferred, with any deposit that may have taken place, into a smaller vessel of glass. Here let it be evaporated to dryness, at a temperature not exceeding 300° Fahrenheit.

(a) The dry mass, when collected and accurately weighed, is to be put into a bottle, and alcohol poured on it, to the depth of an inch. After having stood a few hours, and been occasionally shaken, pour the whole on a filter, wash it with a little more alcohol, and dry and weigh the remainder.

(b) To the undissolved residue, add eight times its weight of cold distilled water; shake the mixture frequently; and, after some time, filter; ascertaining the loss of weight.

(c) Boil the residuum, for a quarter of an hour, in somewhat more than 500 times its weight of water, and afterwards filter.

(d) The residue, which must be dried and weighed, is no longer soluble in water or alcohol. If it has a brown colour, denoting the presence of iron, let it be moistened with water, and exposed to the sun's rays for some weeks. Or if so long a process be inconvenient, moisten it with nitric acid, and then dry and ignite it. This will peroxidize the iron.

I. The solution in alcohol (a) may contain one or all of the following salts: Murates of lime, magnesia, alumina, or

baryta; or nitrates of the same earths. Sometimes, also, the alcohol may take up a sulphate of iron, in which the metal is oxidized to the maximum. This will appear from its reddish brown colour.

1. In order to discover the quality and quantity of the ingredients, evaporate to dryness; weigh the residuum; add above half its weight of strong sulphuric acid; and apply a moderate heat. The muriatic or nitric acid will be expelled, and will be known by the colour of their fumes; the former being white, and the latter orange coloured.

2. To ascertain whether lime or magnesia be the basis of the salts, let the heat be continued till no more fumes arise, and let it then be raised, to expel the excess of sulphuric acid. To the dry mass, add twice its weight of distilled water. This will take up the sulphate of magnesia, and leave the sulphate of lime. The two sulphates may be separately decomposed, by boiling with three or four times their weight of carbonate of potassa. The carbonates of lime and magnesia, thus obtained, may be separately dissolved in muriatic acid, and evaporated. The weight of the dry salts will inform us how much of each the alcohol had taken up. Lime and magnesia may also be separated by the use of the phosphate of soda, applied in the manner already described, (No. XIX.) Alumina and magnesia may be separated from each other, by adding to their mixed and heated solutions an excess of potassa, which will dissolve the alumina only.

The presence of baryta, which is very rarely to be expected, may be known by a precipitation ensuing on adding sulphuric acid to a portion of the alcoholic solution, which has been diluted with 80 or 100 times its bulk of pure water.

Some of the salts obtained by the action of alcohol, it is supposed by Grotthus, are actually formed by its operation. Sulphate of soda and muriate of magnesia, for example, when found in an alcoholic solution, result, he believes, from the mutual decomposition of sulphate of magnesia and muriate of soda. (Ann. de Chim. et de Phys. iv. 366.)

II. The watery solution (*b*) may contain a variety of salts, the accurate separation of which from each other is a problem of considerable difficulty. The number, however, of salts that are capable of existing together in solution is much limited by the mutual action of several in decomposing each other. Such

salts are said to be *incompatible*. A table of them is inserted in the Appendix, which it is proper that the reader should consult, when engaged in analyzing any mixed saline solution.

1. The analysis of a saline solution may be attempted by crystallization. For this purpose, let one half be evaporated by a very gentle heat, not exceeding  $80^{\circ}$  or  $90^{\circ}$  Faht. Should any crystals appear on the surface of the solution, while hot, in the form of a pellicle, let them be separated and dried on bibulous paper. These are chloride of sodium or common salt. The remaining solution, on cooling very gradually, will, perhaps, afford crystals sufficiently distinguishable by their form and other qualities. When various salts, however, are contained in the same solution, it is extremely difficult to obtain them distinct enough in their forms to ascertain their species.

2. The nature of the saline contents must, therefore, be examined by tests or re-agents.

The presence of an uncombined alkali will be discovered by the stained papers (II), and of acids by the tests (I). The vegetable alkali, or potassa, may be distinguished from the mineral or soda, by saturation with sulphuric acid, and evaporation to dryness; the sulphate of soda being much more soluble than that of potassa; or, by supersaturation with tartaric acid, which gives a soluble salt with soda, but from those of potassa throws down an insoluble bi-tartrate of that base. Chloride of platinum, also, is an excellent test of potassa and its combinations; for, with the smallest portion of this alkali, or any of its salts, it forms a distinct and immediate precipitate, while it is not at all affected by soda or its compounds.

If neutral salts be present in the solution, we have to ascertain both the nature of the acid and of the basis. This may be done by attention to the rules already given for the application of tests, which it is unnecessary to repeat in this place. (See the Table, page 564).

III. The solution by boiling water contains scarcely any thing beside sulphate of lime.

IV. The residuum (*d*) is to be digested in weak acetic acid, which takes up magnesia and lime, but leaves, undissolved, alumina, silica, and peroxide of iron. Evaporate the solution to dryness. If it contain acetate of lime only, a substance will be obtained which does not attract moisture from the air; if

magnesia be present, the mass will deliquesce. To separate the lime from the magnesia, proceed as in I.

The residue, insoluble in acetic acid, may contain alumina, iron, and silica. The two first may be dissolved by muriatic acid, from which the iron may be first precipitated by prussiate of potassa, and the alumina afterwards by ammonia.

*Dr. Murray's Formula for the Analysis of Mineral Waters.*

Some ingenious views respecting the analysis of mineral waters were, several years ago, taken by the late Dr. Murray, of Edinburgh. (Edinb. Transact. viii. 250, or Thomson's Annals.) In proceeding by the method of evaporation, the salts obtained are frequently, he conceived, the products of the operation, and not the original ingredients of the water. For example, though we may obtain from a mineral water sulphate of lime and muriate of soda, yet it is probable, he thinks, that the water, in its natural state, held in solution both sulphate of soda and muriate of lime, which, though incompatible salts, when mingled together in dense solution, may yet exist without mutual decomposition, when diffused through a large quantity of fluid. He argues, therefore, that we attain a much nearer approximation to the true composition of a mineral water by disregarding entirely the salts resulting from its evaporation; and, instead of this, determining with extreme precision the elements, or acids and bases, of which those salts are composed. The peculiar mode of combination, in which they exist in the water submitted to analysis, can only, he thinks, be inferred by considering the most probable views of their binary composition.

Having gained a general idea of the nature of any mineral water, by the agency of the tests already described, Dr. Murray recommends that we proceed to its minute analysis in the following manner:

1. Reduce the water, by evaporation, as far as can be done without occasioning any sensible precipitation or crystallization.
2. Add muriate of baryta (or solution of chloride of barium) as long as it occasions a precipitate, and no longer. By an experiment on a separate quantity, examine whether the precipitate effervesces with dilute muriatic acid, and whether it is entirely dissolved by that acid or not. If entirely soluble, dry and weigh it, and allow 22 grains of carbonic acid for every 100 grains. If it do not effervesce, or dissolve, we may consider it

as sulphate of baryta, and reckon that it contains, in a dry state, 34 grains of sulphuric acid in every 100. If it be partly soluble with effervescence, and partly insoluble, it consists both of carbonate and sulphate of baryta, the former of which may readily be separated from the latter by diluted muriatic acid; and the precipitate being weighed in a dry state, both before and after the action of the acid, we learn the quantity of each, what remains being the sulphate only.

By evaporation, the *carbonic acid* is expelled, and the *sulphuric acid* is separated by the barytic salt. The next object is to discover the kind and quantity of the bases present; and then to find the quantity of muriatic acid originally contained in the water.

3. To the clear liquor add a saturated solution of oxalate of ammonia, as long as any turbid appearance is produced. Collect the precipitate, which consists of oxalate of lime; dry it; and, by calcining it at a low red heat, convert it into a carbonate, which may be changed into sulphate by a slight excess of sulphuric acid. The sulphate, after ignition, contains, in 68 parts, 28 of lime, or 41.5 per cent.

4. The next step is to separate the *magnesia*, which may be done as follows: let the clear liquid, remaining after the precipitation of the oxalate of lime, be heated to 100° Fahrenheit, and, if necessary, reduced a little by evaporation; and then add to it, first a solution of carbonate of ammonia, and afterwards of phosphate of ammonia, as long as any precipitation ensues. Wash the precipitate, dry and calcine it at a red heat for an hour, after which 100 grains may be estimated to contain 40 or 41 of magnesia.

5. To estimate the *soda*, evaporate the liquor remaining after the preceding operations to dryness, and expose the dry mass to heat as long as any vapours exhale, raising it, in the end, to redness. The residual matter is chloride of sodium, 60 parts of which are equivalent to 24 sodium, 36 chlorine, according to the view now universally adopted respecting common salt, which, however, is still regarded by some chemists as muriate of soda, when dissolved in water, and then only.

6. It is possible that the chlorine, deduced from the residuary common salt, or rather the muriatic acid which it forms with hydrogen, may exceed the true quantity, and that a part may have been introduced by the muriate of baryta. Or, on the

other hand, if muriate of lime or of magnesia were present in the water, the ammonia, by which those earths were separated, would form, with the muriatic acid, detached from those bases, a salt, which may have been dissipated by heat; and consequently the chlorine or muriatic acid will have been stated too low. To decide this, the simple rule is, to suppose the elements, obtained by the analysis, combined in binary compounds according to the known proportions in which they unite. The excess or deficiency of chlorine or muriatic acid will then appear; and the amount of the excess, being subtracted from the quantity of chlorine or muriatic acid existing in the common salt; or the amount of the deficit, being added to that quantity, the real quantity of chlorine or muriatic acid will be apparent.—As a check on this operation, it may be proper to estimate directly the quantity of chlorine or muriatic acid in a given portion of the water, by first abstracting any sulphuric or carbonic acid by nitrate of baryta, and then precipitating the chlorine by nitrate of silver. The real quantity of chlorine, and its equivalent of muriatic acid, will thus be found, (see p. 144 of this vol.); and the result will form a check on the other steps of the analysis; for the other ingredients must bear that proportion to the muriatic acid which will correspond with the state of neutralization.

Having thus discovered the different acids and bases, and determined their quantities, it remains to determine the state of combination in which they exist. They may either be considered as forming simultaneous combinations, or as existing in the state of binary compounds. In the latter case, it is probable that the acids and bases are so united as to form the most soluble compounds, and in this way we may state them. It may also be proper to give the quantity of binary compounds obtained by evaporation, or by any other direct analytic process. For example, the elements of the salts in a pint of sea-water, as determined by Dr. Murray's analysis, (Edin. Phil. Trans.) are,

Lime . . . . .	2.9 grains
Magnesia . . . . .	14.8
Soda . . . . .	96.3
Sulphuric acid . . . .	14.4
Muriatic acid . . . .	97.7 (=95.06 chlor. + 2.64hydr.



The compound salts, as obtained by evaporation, are,

Chloride of sodium	180.5 grains
Muriate of magnesia	23.
Sulphate of magnesia	15.5
———— lime . . . .	7.1
	<hr/>
	226.1

But the salts existing in a wine-pint of sea-water, in its natural state, before subjecting it to evaporation, may be calculated to be

Chloride of sodium	180.5 grains
Muriate of magnesia	18.3
———— lime . . . .	5.7
Sulphate of magnesia	21.6
	<hr/>
	226.1

The specific gravity of sea-water varies from 1.0269 to 1.0285; that of inland seas is still higher, of the Dead Sea, for example, 1.211. Beside the ingredients enumerated in the Table, sea-water contains minute quantities of hydriodic and hydrobromic acids, and also of potassa.

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### SECTION III.

#### *Examination of Minerals.—General Directions.*

The chemical analysis of minerals is attended even with greater difficulties than that of natural waters; and it would require not only a separate work, but one of considerable extent, to lay down rules for determining the proportions of all possible combinations. The art of separating bodies from each other depends, indeed, upon an extensive and profound knowledge of general chemistry, especially in cases where a great variety of substances are united in the subject of analysis. On the present occasion, I mean only to offer a few general directions for attaining such a knowledge of the composition of mineral bodies as may enable the chemical student to refer them to their proper place in a mineral arrangement, and to judge whether or not they may admit of application to the uses of common life. Those who are solicitous to become adepts in the art of mineral analysis, should study attentively the particular

examples of this sort of research by analysts of great experience, which are dispersed through various periodical works. An admirable work of M. Klaproth, entitled, "Analytical Essays towards improving the Chemical Knowledge of Minerals," 2 vols. 8vo. published in London in 1801, may be consulted with advantage; and in Mr. Children's work on chemical analysis, chiefly translated from Thenard, as well as in an 8vo. volume of Berzelius, entitled "*De l'Analyse des Corps Inorganiques*," published at Paris in 1827, the reader will find a collection of excellent rules and examples for guiding and assisting his researches. These rules must of course be modified, to suit the ever-varying circumstances, to which they are applicable in a general way.

The great variety of mineral bodies, which nature presents in the composition of this globe, may, conveniently for our present purpose, be arranged under four heads. 1st, EARTHS; 2d, SALTS; 3d, INFLAMMABLE FOSSILS; and 4th, METALS, and their Ores.

I. EARTHS. The term *earth*, we may use with Mr. Kirwan, to denote a tasteless, inodorous, dry, brittle, unflammable substance, whose specific gravity does not exceed 4.9 (*i. e.* which is never five times heavier than water), and which gives no tinge to borax in fusion. Some exceptions to this definition are afforded by the strong state of certain earths, and the solubility of others when uncombined; but since a line must be drawn between salts and earths, it may begin where solution is scarcely perceptible; salts terminating, and earths, in strictness, commencing, where the weight of the water, requisite for the solution, exceeds that of the solvent 500 times. Not to depart, however, too widely from the commonly received import of words that are in constant use, substances that require 100 times their weight of water to dissolve them, and have the other sensible properties of earths, may be so styled in a loose and popular sense.

The *simple*, or *primitive earths*, are those which can only be resolved into oxygen and a metallic basis. Such are lime, magnesia, alumina, silica, &c.

The *compound earths* are composed of two or more primitive earths, united chemically together. Sometimes the union of an earth with an acid, though strictly a salt, constitutes what in common language is called an earth; as in the examples of sulphate of baryta, fluuate of lime, &c.

II. SALTS. Under this head may be arranged all those substances that require less than 100 times their weight of water to dissolve them. This description, though by no means so amply characteristic of the class of salts as to serve for an exact definition, is sufficient for our present purpose.

III. By INFLAMMABLE FOSSILS, are to be understood all those of mineral origin, whose principal character is inflammability; a criterion which excludes the diamond and metallic substances, though also susceptible of combustion.

IV. METALLIC SUBSTANCES are sufficiently characterized by the external properties enumerated in Chapter IX. Those on which nature has bestowed their proper metallic appearance, or which are alloyed only with other metals or semi-metals, are called *native* metals. But those that are distinguished, as they commonly are in mines, by combination with some other unmetallic substances, are said to be *mineralized*. The substance that sets them in that state is called a mineralizer; and the compound of both *an ore*. Thus, in a certain ore of copper, that metal is found combined with sulphur. The copper may be said in this instance, to be *mineralized* by sulphur, and the compound of the two bodies is called an *ore of copper*.

ART. I.—*Method of examining a Mineral, the Composition of which is unknown.*

A MINERAL substance, presented to our examination without any acquaintance with its composition, should first be referred to one of the above four classes, and a knowledge should be gained of the kind and number of its components, before we proceed to the more difficult task of determining their proportions to each other. To the former class of experiments, the name of *qualitative analysis* has been given; to the latter that of *quantitative*. As a check upon the latter, it is important to examine the coincidence of its results with the atomic weights of the several constituents; for the best and most refined analyses tend to show that the component parts of all well-characterized minerals are in true atomic proportions. This remark is true, not only of crystallized bodies of limited magnitude, but of the vast rocks and extensive strata, which compose the principal part of the crust of our globe.

I. To ascertain whether the unknown mineral contain saline matter, let 100 grains, or any other determinate quantity, in the

state of fine powder, be dried at a known temperature, not exceeding in general  $212^{\circ}$  F., and the loss of weight be carefully ascertained. If any odour should arise from the mineral, when drying, or if its vapour act on moistened test papers, it may be advisable to collect the condensible product by using a retort and receiver, and to examine its nature. Gaseous fluids are sometimes evolved, also, and when this occurs, a retort of green glass may be used to contain the mineral, and the heat of a spirit lamp be applied, the gases being received over mercury. The remainder (or, if it be preferred, 100 grains of the dried powder) may be put into a bottle, and shaken up repeatedly, with 30 times its weight of water, of the temperature of  $120$  or  $130^{\circ}$ . After having stood an hour or two, pour the contents of the bottle on a filtering paper, previously weighed and placed on a funnel, and wash it with abundance of cold distilled water, which should be directed on the edges of the filter. When the water has drained off, dry the powder on the filtering paper, in a heat of about  $212^{\circ}$ ; and, when dry, let the whole be accurately weighed. If the weight be considerably less than the joint weight of the powder before digestion and the filtering paper, we may infer that some salt has been dissolved, and the decrease of weight will indicate its quantity. In the instance of difficultly-soluble salts, repeated portions of boiling water are necessary.

Should the mineral under examination be proved, by the foregoing experiment, to contain much saline matter, the kind and proportion must next be determined, by rules which will hereafter be laid down.

II. The second class, *viz.*, earthy bodies, are distinguished by their insolubility in water, by their freedom from taste, by their uninflammability, and by their specific gravity never reaching 5. If, therefore, a mineral be insoluble in water, when tried in the foregoing manner; and if it be not consumed, either wholly or in considerable part, by keeping it, for some time, on a red-hot iron; we may conclude that it is neither a salt nor an inflammable body.

III. The only remaining class with which it can be confounded is that of ores of metals, from many of which it may be distinguished merely by poisoning it in the hand, the ores of metals being always heavier than earths; or, if a doubt should still remain, it may be weighed hydrostatically. The mode of

doing this it may be proper to describe. Let the mineral be suspended by a piece of fine hair, silk, or thread, from the scale of a balance, and weighed in the air. Suppose it to weigh 250 grains. Let it next (still suspended from the balance) be immersed in a glass of distilled water, of the temperature of 60° Fahr. The scale containing the weight will now preponderate. Add, therefore, to the scale from which the mineral hangs, as many grain-weights as are necessary to restore the equilibrium. Suppose that 50 grains are necessary, then the specific gravity may be learned by dividing the weight in air by the weight lost in water. Thus, in the foregoing case,  $250 \div 50 = 5$ ; or, a substance which should lose weight in water, according to the above proportion, would be five times heavier than water. It must, therefore, contain some metal, though probably in no great quantity. Any mineral, which, when weighed in the above manner, proves to be 5, 6, 7, or more times heavier than water, may, therefore, be inferred to contain a metal, and may be referred to the class of ores. For determining the specific gravity of powders, an instrument has been contrived by Professor Leslie, to which he has given the name of *coniometer*. It is described in the Ann. of Phil. 2d Series, xi. 313.

IV. Inflammable substances are distinguished by their burning away, either entirely or in considerable part, on a red-hot iron; and by their detonating, when mixed with powdered nitre, and thrown into a red-hot crucible. Certain ores of metals, however, which contain a considerable proportion of inflammable matter, answer to this test, but may be distinguished from purely inflammable substances by their greater specific gravity.

I shall now proceed to offer a few general rules for the more accurate examination of substances of each of the above classes.

#### ART. II.—*Examination of Salts.*

1. A solution of saline matter, obtained in the foregoing manner, may be slowly evaporated, and left to cool gradually. When cold, crystals will probably appear, which a chemist, acquainted with the forms of salts, will easily recognise. But, as several different salts may be present in the same solution, and may not crystallize in a sufficiently distinct shape, it may be necessary to have recourse to the evidence of tests.

2. Let the salt, in the first place, be referred to one of the following orders :

(a) *Acids, or salts with excess of acid.* These are known by their effect on blue vegetable colours. The particular species of acid may be discovered by the tests enumerated in the Table, p. 564.

(b) *Alkalis.* These are characterized generally by their effect on vegetable colours, p. 545, and the species may be discriminated by the tests p. 565.

(c) *Salts with metallic bases.* Metallic salts afford a very copious and generally a coloured precipitate, when mixed with a solution of ferro-cyanate of potassa. (See Table, vol. i. p. 574.) To ascertain the species of metal, precipitate the whole by the ferro-cyanate, calcine the precipitate, and proceed according to the rules which will hereafter be given for separating metals from each other.

(d) *Salts with earthy bases.* If a solution of salt, in which ferro-cyanate of potassa occasions no precipitation, afford a precipitate, immediately on adding pure or carbonated potassa, we may infer, that a compound of an acid, with some one of the earths, is present in the solution. Or, after ferro-cyanate of potassa has ceased to throw down a sediment, if the above-mentioned alkali precipitates a farther portion, we may infer that both earthy and metallic salts are contained in the solution.

In the first case, add the alkaline solution, and, when it has ceased to produce any effect, let the sediment subside, decant the supernatant liquor, and wash and dry the precipitate. The earths may be examined, according to the rules that will be given in the following article. In the second case, ferro-cyanate of potassa must be added, as long as it precipitates any thing, and the liquor must be decanted from the sediment, which is to be washed with distilled water, adding the washings to what has been poured off. The decanted solution must next be mixed with the alkaline one, and the precipitated earths reserved for experiment. By this last process, earths and metals may be separated from each other.

(e) *Neutral salts with alkaline bases.* These salts are not precipitated either by ferro-cyanate or by carbonate of potassa. It may happen, however, that salts of this class may be contained in a solution, along with metallic or earthy ones. In this case the analysis becomes difficult; because the alkali, which is added to precipitate the two last, renders it difficult to ascertain whether the neutral salts are owing to this addition, or

were originally present. I am not aware of any method of obviating this difficulty, except the following: Let the metals be precipitated by ferro-cyanate of ammonia, and the earths by carbonate of ammonia, in a temperature of  $180^{\circ}$  or upwards, in order to ensure the decomposition of magnesian salts, which this carbonate does not effect in the cold. Separate the liquor by filtration, and boil it to dryness. Then expose the dry mass to such a heat as is sufficient to expel the ammoniacal salts.\* Those with bases of fixed alkali will remain unvolatilized. By this process, indeed, it will be impossible to ascertain whether ammoniacal salts were originally present; but this may be learned by adding to the salt under examination, before its solution in water, some pure potassa, which, if ammonia be contained in the salt, will produce the peculiar smell of that alkali. The vegetable and mineral alkalis may be distinguished by adding to the solution a little tartaric acid, which precipitates the former but not the latter; or by muriate of platinum, which acts only on the vegetable alkali.

Having ascertained the basis of the salt, the acid will easily be discriminated. Muriated baryta will indicate sulphuric acid; nitrate of silver the muriatic; and salts containing nitric acid, may be known by a detonation ensuing on projecting them, mixed with powdered charcoal, into a red-hot crucible.

### ART. III.—*Examination of Earths and Stones.*

When a mineral, the composition of which we are desirous to discover, resists the action of water, and possesses characters that rank it among earthy bodies, the next object of inquiry is the nature of the earths that enter into its composition; in other words, how many of the simple earths, and which of them, it may contain.—Of these earths (*viz.*, silica, alumina, magnesia, lime, strontia, baryta, zirconia, glucina, and yttria), one or more may be expected in the composition of a mineral, beside a small proportion of metals, to which the colour of the stone is owing. In general, however, it is not usual to find more

\* This application of heat will drive off, also, any excess of the ammoniacal carbonate, which might have retained in solution either yttria, glucina, or zirconia. The alkaline salts may be separated from these earths, by boiling the mixture in water, filtering, and evaporating.

than four of the simple earths in one mineral. The last-discovered alkali, lithia, and the earths, zirconia, glucina, and yttria, occur very rarely.

A stone which is intended for chemical examination, should be finely powdered in a mortar, and care should be taken that the mortar is of harder materials than the stone, otherwise it would be liable to abrasion, and uncertainty will be occasioned in the result of the process. A longer or shorter time is required, according to the texture of the stone. Of the harder gems, 100 grains require two or three hours' trituration. For soft stones, a mortar of Wedgwood's ware is sufficient; but, for very hard minerals, one of agate, or hard steel, is required; and the stone should be weighed both before and after pulverization, that the addition, if any, may be ascertained and allowed for. Gems, and stones of equal hardness, gain generally from 10 to 13 per cent. When a stone is extremely difficult to be reduced to powder, it may sometimes be necessary to make it red-hot, and while in this state to plunge it into cold water. By this process it becomes brittle, and is afterwards easily pulverized. But this treatment is not always effectual; for Klaproth found the hardness of corundum not at all diminished by igniting it, and quenching in cold water.

The chemical agents, employed in the analysis of stones, should be of the greatest possible purity. To obtain them in this state, directions have been given in the former part of this work.

In treating of the analysis of stones, it may be proper to divide them, 1st, into such as are soluble, either wholly or in part, and with effervescence, in nitric or muriatic acids, diluted with five or six parts of water; and, 2dly, into such as do not dissolve in these acids.

### 1. *Earths or Stones, soluble with Effervescence, in Acids.*

(A) If it be found, on trial, that the mineral under examination effervesces with diluted nitric or muriatic acid, let a given weight, finely powdered, be digested with one of them, in a gentle heat, for two or three hours. A mixture of the two acids is, in some cases, preferable to either separately, as it acts best on substances, which require to be oxidized before they can be dissolved. Sulphuric acid is best adapted for stones of the



magnesian kind. When all action appears to have ceased, filter the solution, reserving the insoluble portion.

(B) The solution, when effected, may contain lime, magnesia, alumina, baryta, or strontia. To ascertain the presence of the two last, dilute an aliquot part of the solution with twenty times its bulk of water, and add a little sulphuric acid, or, in preference, solution of sulphate of soda. Should a white precipitate fall down, we may infer the presence of baryta, of strontia, or of both.

(C) To ascertain which of these earths (*viz.*, baryta or strontia) is present, or, if both are contained in the solution, to separate them from each other, add sulphate of soda to a very dilute solution, till the precipitate ceases; decant the supernatant liquid; wash the sediment on a filter, and dry it.—Then digest it, with four times its weight of sub-carbonate of potassa, and a sufficient quantity of water, in a gentle heat, during several hours. A double exchange of principles will ensue, and we shall obtain a carbonate of baryta or strontia, or a mixture of both, with some undecomposed sulphate. Pour on these, after being well washed, nitric acid, of the specific gravity 1.4, diluted with an equal weight of distilled water. This will dissolve the strontia, but not the baryta. To determine whether any strontia has been taken up by the acid, evaporate the solution to dryness, and dissolve the dry mass in alcohol. This alcoholic solution, if it contain nitrate of strontia, will burn with a deep blood-red flame.

Baryta and strontia may also be separated from each other in the following manner: To a saturated solution of the two earths in an acid, add ferro-cyanate of potassa, which, if pure, will occasion no immediate precipitation; but, after some time, small and insoluble crystals will form on the surface of the jar. These are the prussiated baryta, which may be changed into the carbonate by a red heat, continued, with the access of air, till the black colour disappears. The strontia may be afterwards separated from the solution by carbonate of potassa.

A third method of separating strontia from baryta is founded on the stronger affinity of baryta, than of the former earth, for acids. Hence if the two earths be present in the same solution, add a solution of pure baryta, till the precipitation ceases. The baryta will seize the acid, and will throw down the strontia. The strontitic solution, in this case, should have no excess of

acid, which would prevent the action of the barytic earth.\* It must be acknowledged, however, that all these methods of separating baryta and strontia from each other are imperfect, and that an effectual process is still a desideratum.

(D) The solution (B), after the addition of sulphate of soda, may contain lime, magnesia, alumina, and some metallic oxides. To separate the oxides, add ferro-cyanate of potassa, till its effects cease, and filter the solution, reserving the precipitate for future experiments.

(E) When lime, magnesia, and alumina, are contained in the same solution, proceed as follows:

(a) Precipitate the solution, previously made hot, by carbonate of potassa; wash the precipitate well, and dry it. It will consist of carbonate of lime, magnesia, and alumina. (b) The alumina may be separated by digestion with a solution of pure potassa; which will dissolve the alumina, but not the other earths. (c) To this solution of alumina, add, very cautiously, diluted muriatic acid, till the precipitate ceases, and no longer: or, as Mr. Chenevix recommends, substitute muriate of ammonia, which throws down the alumina, without risk of redissolving it; decant the supernatant liquor; wash the precipitate well with distilled water, and dry it. Then expose it to a low red heat, in a crucible, and weigh it, which will give the proportion of alumina.

(F) Magnesia and lime may be separated, though not with perfect accuracy, by the following process: Evaporate to dryness the solution in nitric or muriatic acid. Weigh the dry mass, and pour on it, in a glass evaporating-dish, † more than its own weight of strong sulphuric acid. Apply a sand-heat till the acid ceases to rise, and then raise the heat, so as to expel the excess of sulphuric acid. Weigh the dry mass, and digest it in twice its weight of cold distilled water.—This will dissolve the sulphate of magnesia, and will leave the sulphate of lime, which must be put on a filter, washed with a little more water, and dried in a low red heat. To estimate the quantity of lime, allow for

\* Klaproth separates baryta from strontia by evaporating the mixed solutions of both. The barytic salt, being less soluble, separates first; and the strontitic is contained in the last portions.

† The bottom of a broken Florence flask answers this purpose extremely well, and bears, without breaking, the heat necessary to expel the sulphuric acid.

that base 41 per cent. of the weight of the precipitate ascertained before it has become cold.

The magnesia is next to be precipitated from its sulphate by the sub-carbonate of potassa, in a heat approaching  $212^{\circ}$ ; and the precipitate, after being well washed, must be dried, and calcined for an hour. Its weight, after calcination, will give the quantity of magnesia contained in the stone.

It had been recommended, when magnesia and lime are contained in the same solution, to precipitate the latter by the bicarbonate of potassa; but it has been shown by Bucholz, that this process is defective (*Ann. de Chim. et de Phys.* iii. 403), a considerable proportion of the carbonate of lime remaining in solution. Doebereiner prefers adding the sub-carbonate of ammonia to the cold solution of the two earths. The carbonate of lime is thus thrown down, and carbonate of magnesia may afterwards be separated, by boiling the liquor; but it is found in practice that the first precipitate contains a little magnesia, and the second a little lime. To obviate this difficulty, both carbonates may be precipitated together by adding sub-carbonate of soda or of potassa to the heated solution; and from this precipitate, after being sufficiently washed, muriate of ammonia will take up the carbonate of magnesia, leaving that of lime separate. From the weights of the carbonates, it is easy to estimate those of the pure earths contained in them.

Mr. Phillips recommends the following plan of separating lime and magnesia from each other: To the muriatic or nitric solution of the two earths, add sulphate of ammonia in sufficient quantity; evaporate the mixture gradually to dryness; and then heat it to redness, till it ceases to lose weight by the volatilization of the muriate or nitrate of ammonia formed. Note the weight of the mixed salt, reduce it to powder, and wash it with a cold saturated solution of sulphate of lime, till all the sulphate of magnesia appears to be dissolved; dry the sulphate of lime left; and by deducting its weight from that of the mixed sulphates, the quantity of sulphate of magnesia dissolved will appear. (*Quart. Journ.* vi. 316.) This method, which it appears had been practised also by Mr. Cooper, has been shown by the latter to be susceptible of great precision. (*Quart. Jour.* vii. 392.)\*

\* Respecting the separation of magnesia and lime from each other, the reader may also consult *Ann. de Chim. et de Phys.* ix. 177, xii. 255, and xvii. 349; also, *Ann. of Phil.* xii. 394, xiii. 58, and Berzelius de l'Analyse, p. 61.

Dr. Daubeny, in an elaborate memoir on the methods of separating lime from magnesia, (Edinburgh Philosophical Journal, vii. 108,) proposes the following modification of the process which has been just described: Dissolve a given portion of the earth under examination in nitric acid, thus separating the silica, and most of the peroxide of iron, from the lime, magnesia, alumina, protoxide of iron, &c. Evaporate the solution, and drive off the nitric acid by heat, thus converting the iron into a peroxide. Weigh the residuum after calcination, and treat it with distilled vinegar or diluted acetic acid, which will take up only the lime and magnesia. Subtract the weight of the undissolved portion from that of the residuum after calcination, thus ascertaining the joint weight of the dissolved lime and magnesia; then decompose the acetates by sulphate of ammonia; evaporate the solution nearly to dryness, and separate the sulphate of magnesia from the sulphate of lime, by washing with water already saturated with sulphate of lime. Expose the sulphate of lime to a red heat, and ascertain its weight, from which the amount of the lime originally present may be readily deduced. We may then infer the weight of the magnesia from the difference between the amount of the lime, and that of the whole which the vinegar was found to have dissolved; or, if we wish to verify the result, it may be done by precipitating the magnesia by an alkali, or still better by converting it into triple phosphate. The quantity of sulphate of lime, present in the water used for washing off the sulphate of magnesia, may be estimated and allowed for.

Or we may content ourselves by dissolving the lime and magnesia in muriatic acid; decomposing the solution by sulphate of ammonia; and after suffering the sulphate of lime to subside, decanting off the supernatant liquor, and throwing down the magnesia from the latter by carbonate of ammonia and phosphate of soda. The magnesia contained in the precipitate may be estimated by the rule already given.

It has been proposed by Mr. John Davies (Ann. of Phil. N. S. viii. 99), to attain the same object by the aid of calculation. By the name of *atomic multipliers*, he designates those numbers, whether whole or fractional, by which, if we multiply the weight of an atom of any base, we shall obtain that of the corresponding salt. Now it appears, from the table of chemical equivalents, that when the number, denoting the weight of an

atom of magnesia is multiplied by 3, and that of an atom of lime by  $\frac{17}{7}$ , we obtain the numbers representing the relative weights of the sulphates of those earths.

Suppose, then, that we have a quantity of lime and magnesia weighing together 96 grains, and that when converted into sulphates, their joint weight is  $265\frac{1}{7}$  grains, it is required to determine by calculation the quantity of each earth.

Assume  $x$  = the quantity of magnesia,

And  $y$  = ————— lime.

Then  $x + y = 96$ ,

And  $3x + \frac{17}{7}y = 265\frac{1}{7}$ .

Hence  $x = 56$ , the quantity of magnesia, and  $y = 40$ , that of lime. A general formula for all similar cases has been given by Mr. Davies in the same essay. The great objection to its application in practice, is the influence of very minute changes of the data in materially altering the results of calculation.

(G) If magnesia and alumina only be held in solution by an acid (the absence of lime being indicated by the non-appearance of a precipitate, on adding oxalate of ammonia), the two earths may be separated by adding to the heated solution, liquid potassa, which throws down the magnesia, and redissolves the alumina. From the alkaline liquid, to which the washings of the precipitated magnesia are to be added, the alumina may be thrown down by muriate of ammonia. Or, to the cold solution of the two earths, we may add carbonate of ammonia, which precipitates carbonate of alumina, leaving that of magnesia dissolved. A complete separation of the two earths is opposed however, by their affinity for each other. Alumina containing not more than 1 per cent. of magnesia, has been observed by Berzelius to have the property, after calcination, of becoming very hot on contact with water.

Magnesia and alumina may, also, be separated by succinate of soda, which precipitates the latter earth only.

When the nitric solution of magnesia, of alumina, or of both, contains a small proportion of iron, this may be separated by evaporating to dryness, calcining the residue, during one hour, in a low red heat, and dissolving again in dilute nitric acid, which does not take up iron when thus per-oxidized.

(H) The insoluble residue (A) may contain alumina, silica,

and oxides of metals, so far oxidized, as to resist the action of nitric and muriatic acids.

(a) Add concentrated sulphuric acid, with a small quantity of sulphate of potassa, and evaporate the mixture to dryness, in a glass or platinum vessel. On the dry mass pour a fresh portion of sulphuric acid; boil again to dryness, and let this be done, repeatedly, three or four times. By this operation, the alumina will be converted into alum, which will be easily soluble in warm water; and from the solution, crystals of alum will shoot on evaporation. The alumina may be precipitated from the sulphuric acid by carbonate of potassa; washed, dried, and ignited; and its weight ascertained.

Klaproth procured crystals of alum from one-fourth of a grain of alumina. The quantity of alumina he estimates at one-tenth the weight of the crystallized alum which is obtained.

During the evaporation of a solution of alumina, which has been separated from silica, portions of the latter earth continue to fall, even to the last. (See Klaproth, vol. i. pages 66 and 75.) These must be collected, and washed with warm water; the collected earth added to the portion (b), and the washings to the solution (a).

Alumina may be separated from oxide of iron by a solution of pure potassa.

From whatever acid alumina is precipitated by a fixed alkali, it is apt to retain a small portion of the precipitant. To ascertain the true quantity of this earth, it must, therefore, be re-dissolved in acetous acid, again precipitated by solution of pure ammonia, dried and ignited.

(b) The oxides (generally of iron only) may be separated from the silica in the following manner: Let the insoluble part (a) be ignited in a crucible with a little wax. This will render the oxides soluble in diluted sulphuric acid, and the silica will be left pure and white. Let it be washed, ignited, and its weight ascertained. The analysis of the mixture of oxides will be described in the paragraph (S).

## 2. *Stones insoluble in diluted nitric and muriatic Acids.*

These stones must be reduced to powder, observing the precautions which have been already given.

(I) Let 100 grains, or any other determinate quantity, be

intimately mixed with three times their weight of pure and dry potassa, or with from 3 to 5 parts of carbonate of that base, which, however, is ill adapted to minerals containing zirconia, or oxides of columbium or tin. Put the whole into a crucible of pure silver, set in one of earthenware of a larger size, the interstices being filled with sand; and add a little water.\* The crucible, covered with a lid, must then be gradually heated; and, as the materials swell and would boil over, they are to be pressed down constantly with a rod or spatula of silver. When the moisture is dissipated, and the mass has become quite dry, raise the heat as far as can be done without melting the crucible; if of silver, and continue the heat during half an hour, or an hour.

The phenomena that occur during this operation indicate, in some degree, the nature of the mineral under examination. If the mixture undergo a perfectly liquid fusion, we may presume that the stone contains much siliceous earth; if it remain pasty and opaque, the other earths are to be suspected; and, lastly, if it have the form of a dry powder, the bulk of which has considerably increased, it is a sign of the predominance of alumina.

If the fused mass have a dark green or brownish colour, the presence of oxide of iron is announced; a bright green indicates manganese, especially if the colour be imparted to water; and a yellowish green the oxide of chrome.

(a) The disintegration of stones, consisting chiefly of alumina, is not easily effected, however, by means of potassa. Mr. Chenevix found (Philosophical Transactions, 1802) that minerals of this class are much more completely decomposed by fusion with calcined borax. One part of the mineral to be examined, reduced to a very fine powder, and mingled with  $2\frac{1}{4}$  or three times its weight of glass of borax, is to be exposed to a strong heat for two hours in a crucible of platinum, set in a

\* Klaproth effected the disintegration of corundum (which resisted eleven successive fusions with alkali) by adding to the powdered stone, in a crucible, a solution of pure potassa, boiling to dryness, and pushing the mixture to fusion. The alkali must be perfectly caustic, and must have been purified by alcohol. A platinum crucible is unfit for this purpose, as it is corroded by pure alkalis. There are other circumstances, enumerated by Berzelius (De l'Analyse, p. 8, note) which render the use of platinum vessels objectionable.

larger earthen one, and surrounded by sand. The crucible and its contents, which adhere very strongly to it, are then to be digested, for some hours, with muriatic acid, by which a perfect solution will be accomplished. The whole of the earthy part is then to be precipitated by sub-carbonate of ammonia; and the precipitate, after being well washed, is to be redissolved in muriatic acid. By this means, the borax is separated. The analysis is afterwards to be conducted nearly in the manner which will presently be described. To this process Berzelius objects that the sparing solubility of boracic acid, disengaged by adding the muriatic, must cause uncertain quantities of it to be mixed with the earths and metallic oxides. He considers, therefore, the use of borax as not to be relied upon for correct quantitative results.

(K) The crucible (I) being removed from the fire, is to be well cleaned on the outside, and set, with its contents, in a porcelain or glass vessel, filled with hot water, which is to be stirred and renewed, occasionally, till the whole mass is detached. The water dissolves a considerable part of the compound of alumina and silica with potassa, and even the whole, if added in sufficient quantity. During cooling, a sediment occasionally forms, in the filtered liquor, of a brownish colour, which is oxide of manganese. (See Klaproth, i. 345, *b*.)

(L) To the solution (K), and the mass that has resisted solution, in the same vessel, add muriatic acid. The first portions of acid will throw down a flocculent sediment, which consists of the earths that were held dissolved by the alkali. Then an effervescence ensues; and a precipitate occurs, which is no sooner formed than it is dissolved. Lastly, the portion that resisted the action of water is taken up, silently if it contain alumina, and with effervescence if it be carbonate of lime.

(M) From the phenomena attending the action of muriatic acid, some indications may be derived. If the solution assume a purplish red colour, it is a sign of oxide of manganese; an orange-red shows iron; and a gold-yellow colour betokens chrome. Freedom from colour proves that the stone contains no metallic ingredients.

(N) When the solution is complete, it is to be evaporated to dryness in a porcelain rather than in a glass vessel. If any thing resist solution, it must be again heated, as before (I), with



potassa. When the liquor approaches to dryness, it assumes the form of a jelly, and must then be diligently stirred till quite dry, and till the fumes of muriatic acid have entirely ceased.

(O) (a) Let the dry mass be digested, at a gentle heat, with three or four pints, or even more, of distilled water, and filtered. (b) Wash what remains on the filter, repeatedly, till the washings cease to precipitate the nitrate of silver, and add the washings to the filtered liquor. (c) Let the residue on the filter be dried and ignited in a crucible. Its weight shows the quantity of silica. If pure, it should be perfectly white, and should give a colourless glass when fused under the blow-pipe with an equal weight of anhydrous carbonate of soda. If coloured itself, or if the glass bead be coloured, an admixture of some metallic oxide is indicated. From this the precipitate may be purified by digestion in muriatic acid, and may again be washed, ignited, and weighed.

(P) (a) The solution (O), which, owing to the addition of the washings, will have considerable bulk, is next to be evaporated, till less than a pint remains; carbonate of potassa must then be added, and the liquor must be heated during a few minutes. Let the precipitate, occasioned by the alkali, subside; decant the liquor from above it, and wash the sediment, repeatedly, with warm water. Let it then be put on a filter, and dried.

(Q) The dried powder (P. a) may contain alumina, lime, magnesia, baryta, or strontia; besides metallic oxides, which may be separated from each other by the rules already given.

(b) Instead of carbonate of potassa, Berzelius adds ammonia in excess, which precipitates the weaker bases, leaving dissolved the baryta, strontia, lime, magnesia, and part of the protoxide of manganese. If the iron be not entirely per-oxidized, a portion of its protoxide remains dissolved, along with the oxides of silver, copper, zinc, cadmium, nickel, and cobalt, if present, and if the ammonia be sufficient for their solution. The separation of the dissolved bases from each other is to be effected by rules which will be presently given.

(R) It may be proper to examine the solution (P) after the addition of carbonate of potassa, in order to discover whether any, and what, acid was contained in the stone.

(a) For this purpose, let the excess of alkali be neutralized by muriatic acid, and the liquor filtered.

(b) Add, to a little of this liquor, a solution of muriated

baryta. Should a copious precipitate ensue, which is insoluble in diluted muriatic acid, the presence of sulphuric acid is detected. And if much baryta, strontia, or lime, has been found in the precipitate (Q), we may infer the presence of a sulphate of one of those earths.

(c) If on mixing the liquid (*a*) with the solution of muriated baryta, a precipitate should ensue which is soluble, without effervescence, in muriatic acid, the phosphoric acid may be known to be present; and, if lime be also found, the phosphate of lime is indicated.

(d) To a portion of the liquor (*a*) add a solution of muriate of lime till the precipitate, if any, ceases. Collect this precipitate, wash it, dry it, and pour on it a little sulphuric acid. Should acid fumes arise, the fluoric acid may be suspected. To ascertain its presence decisively, distil a portion of the precipitate with half its weight of sulphuric acid. The fluoric acid will be known by its effects on the retort, and by its other properties.

(S) The method of separating, from each other, the metallic oxides, usually found as the colouring ingredients of stones, remains to be accomplished.

(a) Let the precipitate by ferro-cyanate of potassa (D), be exposed to a red heat, by which the prussic acid will be decomposed. The oxides thus obtained, if insoluble in dilute nitric or muriatic acid, will be rendered soluble, by again calcining them with the addition of a little wax or oil.

(b) Or the process may be varied by omitting the precipitation by ferro-cyanate of potassa, and proceeding as directed (E). The oxides will remain mixed with the magnesia and lime, and, after the addition of sulphuric acid, will be held in solution by that acid, along with magnesia only.

In both cases the same method of proceeding may be adopted; such variation only being necessary as is occasioned by the presence of magnesia in the latter.

(c) To the solution (*a* or *b*), containing several metallic oxides dissolved by an acid, add a solution of bi-carbonate of potassa, as long as any precipitation ensues. This will separate the oxides of iron, chrome, and nickel; but the oxide of manganese and the magnesia, if any be present, will remain dissolved.

If a small quantity of oxide of manganese be suspected in an oxide of iron, it may be detected by mixing the oxide with nitre, and throwing the mixture into a red-hot crucible. Manganese

will be indicated by an amethystine red tinge in the solution of this nitre.

To separate the oxides of iron and manganese from each other, Gehlen recommends succinic acid, which is preferred, also, by Klaproth and Bucholz. Berzelius employs for this purpose the succinate of soda, and gives minute directions for its successful application. (*De l'Analyse*, p. 47.) Dr. John advises the addition of oxalate of potassa to the solution of the two oxides, first rendered as neutral as possible; but Bucholz finds that this process is imperfect, and that the oxalates precipitate manganese as well as iron.

Mr. Hatchett long ago suggested the following method of separating iron from manganese. The solution of the ore, made by sulphuric acid, and filtrated, must be diluted with three or four pints of cold distilled water. To this liquid, pure ammonia must be gradually added, till it slightly restores the blue colour of reddened litmus paper. The oxide of iron will thus be separated, and will remain on the filter upon which the liquor is thrown; and the oxide of manganese will pass through it, in a state of solution. The oxide of manganese may be obtained by evaporation to dryness, and by calcining in a heat sufficient to expel the muriate of ammonia. (*Thomson's Annals*, v. 343.) The advantage of this method is, that the triple sulphate of ammonia and manganese, being very soluble in water, is not affected by an excess of alkali, so that no nicety is required in the addition of the ammonia. At the same time, Mr. Faraday observes, it is necessary that there be sulphuric acid enough present to form, with the ammonia and the manganese, the soluble triple salt. If to a solution containing much manganese and little iron, excess of ammonia be added, manganese will be thrown down as well as iron, because the sulphuric acid present is not sufficient to combine with the manganese and the ammonia, in the proportions required to convert the whole of the manganese into a triple salt. In such a case, sulphuric acid ought to be added to the solution before the ammonia. When the proportion of iron is greater, of course there is more sulphuric acid present to combine with the ammonia, and less additional acid is required. (*Quart. Jour.* vi. 154.)

Some other methods of separating iron and manganese, in addition to that of Mr. Hatchett, have been described by Mr. Faraday in the same volume of the *Quarterly Journal*, p. 357.

One of the most easy and simple seems to be, to throw down the oxides (the iron being peroxidized) together from their solution; to wash them by decantation; and to digest them in muriate of ammonia with a little sugar. The manganese, both protoxide and peroxide, will be dissolved, and the oxide of iron will remain.

Of these methods of separating iron and manganese, it is probable that Mr. Herschell was not aware, when (in a paper published in the *Annals of Philosophy*, N. S. iii. 95) he condemned as ineffectual all methods antecedent to the following, which he has himself proposed. The solution containing iron is to be brought to the maximum of oxidation, capable of being communicated by boiling with nitric acid. It is then to be just neutralized, *while in a state of ebullition*, by carbonate of ammonia. The whole of the iron to the last atom is precipitated; and the whole of the other metals present (supposed to be manganese, cerium, nickel, and cobalt), remains in solution. To insure success, it is necessary that no oxide of manganese or cerium, above the first degree of oxidation, should be present; otherwise it will fall down along with the iron. In performing the process, the metallic solution should not be too concentrated, and must be agitated the whole time, especially towards the end; and when the tests of alkalis are feebly affected, the ammoniacal carbonate must be added slowly, and in a diluted state. The precipitation turns on a peculiarity in the peroxide of iron, by virtue of which it is incapable of existing in a neutral solution at a boiling temperature. It may be made, Mr. Herschell finds, the principle of a method of detecting the minutest quantity of other metals in union with iron, for example, of nickel, titanium, and manganese, but not of uranium. To this process, Berzelius objects that when the liquid contains, along with peroxide of iron, a fixed acid, such as the phosphoric, boracic, or arsenic, the acid is apt to be thrown down along with the peroxide, and requires to be afterwards separated.

Lastly, M. Quesneville has recently proposed to separate iron from manganese by arseniate of potassa, which precipitates the iron only in the state of an arseniate, decomposable by heat. (*Phil. Mag. and Ann. of Phil.* i. 72, or *Quart. Jour. N. S.* i. 235.)

(d) Magnesia and oxide of manganese may be separated by adding to their solution (c) the hydro-sulphuret of ammonia, which will throw down the manganese, but not the magnesia.

The precipitated sulphuret of manganese has a pale brick hue if pure, or a deeper tinge if iron be present. It must be calcined with the access of air and weighed. The magnesia may afterwards be separated by solution of pure potassa, or of the subcarbonate, at a boiling heat, and, when precipitated, must be washed, dried, and calcined.

(e) The oxide of chrome may be separated from those of iron and nickel, by repeatedly boiling the three to dryness, with nitric acid. This will acidify the chrome, and will render it soluble in pure potassa, which does not take up the other oxides. From this combination with potassa the chromic oxide may be detached by adding muriatic acid and evaporating the liquor till it assumes a green colour. Then, on adding a solution of pure potassa, the oxide of chrome will fall down, because the quantity of oxygen, required for its acidification, has been detached by the muriatic acid.

(f) The oxides of iron and nickel are next to be dissolved in muriatic acid; and the solution evaporated to dryness. Liquid ammonia is then to be added, which acts on the oxide of nickel only. The solution may be again evaporated to dryness, which will render the oxide of iron more dense, and more easily separable from the soluble portion. A fresh addition of ammonia will now readily dissolve the nickel, leaving the oxide of iron, which must be collected on a filter, dried, and weighed. If highly oxidized, it must, before weighing, be calcined with wax, in a crucible.\* The oxide of nickel remains dissolved by the excess of ammonia, to which it imparts a blue colour. It may be separated by evaporating the solution to dryness and dissolving the salt.†

(g) Oxide of nickel may be separated from oxide of copper, when contained in the same solution, by immersing in the solution a bar of zinc, which will precipitate the latter metal only.

(h) From the ammoniacal solution of nickel and cobalt, Mr. Phillips finds that the former metal is immediately precipitated

\* Dr. Marcet alleges that after this operation, the iron still remains in the state of peroxide. (Geolog. Transact. i.) It is by no means easy to decide in what state of oxidation iron exists in minerals. (See Berzelius, p. 54.)

† For an example of the separation of nickel from iron, see Klaproth's Contributions, vol. i. page 422; where, also, and page 428, is an instance of the testing of nickel for copper.

by potassa or soda, which very slowly and sparingly throw down cobalt from the same solvent. Laugier has proposed a method of separating nickel from cobalt, founded on the solubility of the triple oxalate of ammonia and cobalt in water. The mixed oxalates of nickel and cobalt, precipitated by an alkaline oxalate, are to be placed in diluted ammonia, which dissolves both. The solution being exposed to the air, in order that the excess of ammonia may escape, the salt of nickel precipitates, while that of cobalt remains in solution.

The analysis of the stone is now completed, and its accuracy may be judged by the correspondence of the weight of the component parts with that of the stone originally submitted to experiment.

It may be proper to observe, that certain stones, which are not soluble in diluted nitric and muriatic acids, may be decomposed by an easier process than that described (A). Among these are the compounds of baryta, strontia, and lime, with acids, chiefly with the sulphuric, fluoric, and phosphoric. The sulphates of baryta, strontia, and lime; the fluuate of lime; and the phosphate of lime; are all found native in the earth, and, except the last, are all insoluble in the above-mentioned acids. They may be known generally by their external characters. The compounds of baryta and strontia have a specific gravity greater than that of other earths, but inferior to that of metallic ores. They have, frequently, a regular or crystallized form, are more or less transparent, have some lustre, and their hardness is such as does not prevent their yielding to the knife. The combinations of lime, with the above-mentioned acids, are distinguished by similar characters, except that they are much less heavy. To the mineralogist, the outward form and characters of these stones are sufficient indications of their composition.

Instead of the fusion with alkali, an easier process may be recommended. Let the mineral under examination be reduced to powder, and be digested, in nearly a boiling heat, during one or two hours, with three or four times its weight of carbonate of potassa, and a sufficient quantity of distilled water. The acid, united with the earth, will quit it and pass to the potassa, while the carbonic acid will leave the alkali and combine with the earth. We shall obtain, therefore, a compound of the acid of the stone with potassa, which will remain in solution, while

the carbonated earths will form an insoluble precipitate; but as already stated (vol. i. p. 73), the decomposition is scarcely ever complete. It is necessary, therefore, to decant the alkaline liquor; to edulcorate the precipitate with water; then to dissolve the earthy carbonates by diluted muriatic or nitric acids; and to treat the portion which resists solution with a fresh quantity of sub-carbonate of potassa. In this way we may proceed, till boiling with mild alkalis produces no more earthy carbonate. The alkaline solution may be assayed to discover the nature of the acid, according to the formula (I); and the earths, dissolved by the acid which has been applied to them, may be separated from each other by the processes (B), &c.

(T) In the foregoing rules for analysis, I have omitted the mode of detecting and separating *glucina*, because this earth is of very rare occurrence. When alumina and glucina are present in a mineral, they may be separated from the precipitate (E a) by pure potassa, which dissolves both these earths. A sufficient quantity of acid is then to be added to saturate the alkali; and carbonate of ammonia is to be poured in, till a considerable excess of this carbonate is manifested by the smell. The alumina is thus separated, but the glucina, being soluble in the carbonate of ammonia, remains dissolved, and may be precipitated by boiling the solution.

(U) Zirconia may be separated from alumina, by boiling the mixed earths with pure soda, which acts only on the latter. (Klaproth, vol. ii. page 213.) From an acid solution containing both earths, the alumina is thrown down by saturated carbonate of potassa, which, when added in excess, re-dissolves the zirconia. Glucina and zirconia, or glucina and yttria, may be separated, when mixed together in solution, by ferro-cyanate of potassa, which has no action on glucina, but precipitates the two other earths.

(V) Cerium, which often accompanies yttria, may be separated by virtue of a property, which its oxides possess, of forming insoluble double salts with sulphate of potassa. A crystal of the latter salt, suspended at the surface of a solution of oxide of cerium in muriatic acid, occasions a precipitate in 24 hours, which, after decanting the supernatant fluid, is to be washed with solution of sulphate of potassa. The double sulphate of potassa and cerium is to be dissolved in hot water, and decom-

posed by caustic potassa, which throws down oxide of cerium. This is to be washed, dried, and weighed. To separate yttria from alumina, precipitate both earths from a solution containing them, by pure ammonia; boil the precipitate in a solution of pure soda, which chiefly takes up alumina; neutralize the solution with sulphuric acid, and add carbonate of soda to the solution, brought to the boiling temperature. A precipitate will ensue, consisting of alumina, with some yttria. To separate the latter earth, dissolve in muriatic acid, and add an excess of carbonate of ammonia, which takes up only the yttria. To ensure, still farther, the purity of the alumina, dissolve the residue in an excess of sulphuric acid, add a small portion of sulphate of potassa, and crystallize the solution. The crystals of alum, that are produced, contain one-tenth of alumina.

(W) The presence of potassa (which has lately been discovered in some stones) may be detected by boiling the powdered mineral, repeatedly to dryness, with strong sulphuric acid. Wash the dry mass with water, add a little excess of acid, and evaporate the solution to a smaller bulk. If crystals of alum should appear, it is an indication of potassa, because alum can never be obtained in a crystallized form, unless an alkali forms part of the compound.

But since a mineral may contain potassa, and little or no alumina, in which case no crystals of alum will appear, it may be necessary, in the latter case, to add a little alumina along with the sulphuric acid. Or the stone may be so hard as to resist the action of sulphuric acid; and it will then be necessary to fuse it, in the manner directed (I), with soda, which has also a solvent power over alumina and silica. The fused mass is to be dissolved in water, and supersaturated with sulphuric acid. Evaporate to dryness, re-dissolve in water; and filter, to separate the silica. Again evaporate the solution, which will first afford crystals of sulphate of soda, and afterwards sulphate of potassa, should the latter alkali be contained in the mineral.

Klaproth first discovered potassa in leucite, on summing up the results of its analysis, which gave a considerable loss of weight. By boiling the stone with diluted muriatic acid, and evaporation, he obtained crystals of muriate of potassa. Another proof of the presence of potassa was, that, when sulphuric acid was boiled with it, the solution gave crystals of alum, to which potassa is essential. He also boiled the stone with muriatic



acid, and, after dissolving the muriate of alumina by alcohol, muriate of potassa remained. The volcanic leucite contained less potassa than other kinds. The same alkali he also detected, afterwards, in lepidolite.

The potassa, contained in sulphate of alumina, may be separated from that earth, by adding a solution of pure baryta as long as any precipitation is produced. The alumina and sulphate of baryta will fall down together, and the potassa will remain in solution. Its presence may be known by the tests, enumerated at page 562.

In certain minerals that gelatinate, when pulverized and exposed to the action of muriatic acid, Dr. Wollaston has pointed out an easy method of detecting alkalis. Expose the gelatinous mass in a watch glass to a temperature not exceeding that of boiling water, until perfectly dry. In this state if potassa or soda be present, small cubic crystals are generally discoverable with the assistance of a lens. In this way, Dr. Clarke was enabled to discover potassa in Gehlenite. (Ann. of Phil. xiv. 450.)

(X) Soda may be detected in a mineral by the following experiments:—Let the powdered stone be treated with sulphuric acid, as in (U); wash off the solution, and add pure ammonia, till the precipitation ceases; then filter, evaporate the solution to dryness, and raise the heat so as to expel the sulphate of ammonia. The sulphate of soda will remain, and may be known by its appropriate characters.

Soda was first found by Klaproth, in chrysolite, in the large proportion of 36 per cent. This analysis was confirmed by Vauquelin, whose mode of separating soda is the one which I now recommend. Both the fixed alkalis have since been frequently discovered in native minerals; *viz.* soda in basalt (Klaproth, ii. 195); in pitch-stone (207); and in kling-stone, amounting to 8 per cent. (182). The same skilful analyst has found potassa in Hungarian pearl stone (263); and, accompanied by soda, in pumice (20).

A method has been proposed by Sir H. Davy, (Phil. Trans. 1805; or Nicholson's Journal, xiii. 86.) for analyzing stones, containing either of the fixed alkalis, by means of the boracic acid. The process is sufficiently simple. One hundred grains of the stone to be examined must be fused, during half an hour, at a strong red heat, with 200 grains of boracic acid.

An ounce and a half of nitric acid, diluted with seven or eight parts of water, must be digested on the mass, till the whole has been decomposed. The fluid must be evaporated, till its quantity is reduced to an ounce and a half, or two ounces.

If the stone contain silica, this earth will be separated by the processes of solution and evaporation. It must be collected on a filter, and washed well with water, till the boracic acid, and all the saline matter, are separated. The fluid, and all that has passed through the filter, must be evaporated to about half a pint; then saturated with carbonate of ammonia; and boiled with an excess of that salt, till all the materials that it contains, capable of being precipitated, have fallen to the bottom of the vessel. The solution must then be passed through a filter, which retains the earths and metallic oxides. It must then be mixed with nitric acid, till it tastes strongly sour, and evaporated till the boracic acid appears free. The fluid must next be evaporated to dryness; when by exposure to a heat of  $450^{\circ}$  Fahrenheit, the nitrate of ammonia will be decomposed, and the nitrate of potassa or soda will remain in the vessel.

The remaining earths and metallic oxides are separated from each other by common processes; *viz.* alumina by solution of potassa; lime by sulphuric acid; oxide of iron by succinate of ammonia; oxide of manganese by hydro-sulphuret of potassa; and magnesia by pure soda.

Berard has found that nitrate of lead may be advantageously employed in the analysis of stones that contain silicated alkali. One part of the stone very finely powdered is to be intimately mixed with two parts of finely powdered nitrate, and one of carbonate, of lead. The whole is to be put into a platinum crucible, which is to be placed in another crucible and covered with a lid. A red heat is to be applied for a quarter of an hour. The fusion takes place without effervescence, and a yellowish or brownish mass is found in fusion on removing the cover. This is to be poured into water, the coldness of which causes it to split into small fragments that are easily attacked by acids, of which nitric acid is the one best adapted to the purpose. With this acid, it is to be boiled, and occasionally stirred and broken down. The silica remains in a viscid state. The oxide of lead is precipitated by sulphuric acid, added till water saturated with sulphureted hydrogen causes no change. The liquid is boiled with carbonate of ammonia, and the precipitate thus formed analyzed

by common methods. Lastly, the liquid is evaporated to dryness; the salts calcined in a platinum crucible; and the residuum collected and weighed. This residue contains the alkali originally present in the mineral in the state of a sulphate, and almost always sulphate of magnesia. It may be analyzed by processes that have been already described, or by others contrived by Berthier, and detailed in his paper. (*Ann. de Chim. et de Phys.* xvii. 28; or *Quarterly Journal*, xii. 169.)

*Table of Substances which may be expected in Earths and Stones, and References to the Means of separating them from each other.*

*Acid*, fluoric, R. d.

phosphoric, R. c.

sulphuric, R. b.

*Alumina* from lime and magnesia, E.

its quantity, E. c.

from magnesia, G.

silica, H. a.

metallic oxides, H. a.

glucina, T.

*Baryta and strontia* from other earths, B.

from strontia, C.

*Cerium*, from yttria and from oxides of iron and manganese  
V. b.

*Chromium* from manganese, &c. S. c.

iron and nickel, S. e.

*Earths* from oxides, D.

*Glucina* from alumina, T.

*Iron* from manganese, S. e.

nickel, S. f.

*Lime* from magnesia, F.

from alumina, E. b.

its quantity, F.

*Magnesia* from lime, F.

alumina, G.

manganese, S. d.

its quantity, F.

*Manganese*, indications of, M.

from iron, chrome, and nickel, S. c.

magnesia, S. d.

*Nickel* from manganese, S. e.

iron, S. f. from copper, S. g. from cobalt, S. h.

*Oxides, metallic*, from earths, D.

from each other, S.

*Potassa* from earths and oxides, W.

*Silica* from alumina, H a.

earths in general, O. c.

oxides, H. b.

*Soda* from earths and oxides, X.

*Strontia*, see *Baryta*.

*Yttria* from alumina, &c. V.

*Zirconia* from alumina, &c. U.

#### ART. 4.—*Analysis of Inflammable Fossils.*

The exact analysis of inflammable fossils is seldom necessary for directing the most beneficial application of them. It may be proper, however, to offer a few general rules for judging of their purity.

##### I.—*Sulphur.*

Sulphur should be entirely volatilized by distillation in a glass retort. If any thing remain fixed, it must be considered as an impurity, and may be examined by the preceding rules.

Sulphur, also, should be totally dissolved by boiling with solution of pure potassa, and may be separated from its impurities by this alkali.

Impure sulphur, consumed by burning in a small crucible, leaves a residue of oxide of iron and silica.

##### II.—*Coals.*

1. The proportion of bituminous matter in coal may be learned by distilling a known quantity, at a heat below redness, in an earthen retort, and collecting the condensible fluids.

2. The proportion of earthy or metallic ingredients may be found by burning the coal with access of air on a red-hot iron. What remains unconsumed must be considered as an impurity, and may be analyzed by the foregoing rules.

3. The proportion of carbon may be ascertained by observing the quantity of nitrate of potassa, which a given weight of the coal is capable of decomposing. For this purpose, let 500 grains, or more, of perfectly pure nitre be melted in a crucible,

and, when red-hot, let the coal to be examined, reduced to a coarse powder, be projected on the nitre, by small portions at once, not exceeding one or two grains. Immediately, when the flame, occasioned by one projection, has ceased, let another be made, and so on till the effect ceases. The proportion of carbon in the coal is directly proportionate to the quantity required to alkalize the nitre. Thus, since 12.709 of carbon are required to alkalize 100 of nitre, it will be easy to deduce the quantity of carbon, in a given weight of coal, from the quantity of nitre which it is capable of decomposing. This method, however, is liable to several objections, which its inventor, Mr. Kirwan, seems fully aware of. (See his *Elements of Mineralogy*, vol. ii. p. 514.)

4. The most accurate mode of analyzing the different varieties of coal is by ignition with peroxide of copper. Examples of this kind of analysis may be consulted in Dr. Thomson's *Memoir* in the 16th volume of *Annals of Philosophy*.

*Plumbago*, or *black-lead*, is another inflammable substance, which it may sometimes be highly useful to be able to identify, and to judge of its purity.—When projected on red-hot nitre, it should detonate; and, on dissolving the decomposed nitre, an oxide of iron should remain, amounting to about one-tenth the weight of the plumbago. Any mineral, therefore, that answers to these characters, and leaves a shining trace on paper, like that of the black-lead pencils, is plumbago.

#### ART. 5.—*Analysis of Metallic Ores.*

The class of metals comprehends so great a number of individuals, that it is almost impossible to offer a comprehensive formula for the analysis of ores. Ores of the same metal, also, as the mineralizing ingredients vary, require very different treatment. Yet some general directions are absolutely necessary, to enable the chemist to judge of the composition of bodies of this class.

The ores of metals may be analyzed in two modes,—in the humid and the dry way. The first is effected by means of acids and of other liquid agents, and may often be accomplished by persons who are prevented by the want of furnaces, and other necessary apparatus, from attempting the second. If sulphur, however, be present in an ore, which may be generally known by its external characters, as described by mineralogical

writers, it impedes the action of acids : it should, therefore, be separated, either by roasting the ore on a muffle, or by projecting it, mixed with twice or thrice its weight of nitre, into a red-hot crucible, and then washing off the sulphate of potassa by hot water.

It is hardly possible to employ any one solvent, which is capable of taking up all the metals. Thus, the nitric acid does not act on gold or platinum ; and the nitro-muriatic, which dissolves those metals, has no solvent action on silver. It will be necessary, therefore, to vary the solvent according to the nature of the ore under examination.

1. For ores of gold and platinum, the nitro-muriatic acid is the most proper solvent. A given weight of the ore may be digested with this acid, as long as it extracts any thing. The solution may be evaporated to dryness, in order to expel the excess of acid, and dissolved in water. The addition of a solution of muriate of tin will show the presence of gold by a purple precipitate ; and platinum will be indicated by a precipitate, on adding a solution of muriate of ammonia. When gold and platinum are both contained in the same solution, they may be separated from each other by the last-mentioned solution, which throws down the platinum, but not the gold. In this way platinum may be detached, also, from other metals.

When gold is contained in a solution, along with several other metals, it may be separated from most of them by adding a dilute solution of sulphate of iron. The only metals which this salt precipitates are gold, palladium, silver, and mercury. (Consult Dr. Bright's account of the processes followed at the gold and silver mines in Hungary, in his Travels through Hungary, &c.; or in the Philosophical Magazine, lii. 8.)

2. For extracting silver from its ores, the nitric acid is the most proper solvent. Nitric acid, however, does not act on horn-silver ore, consisting chiefly of chloride of silver, which must be decomposed by carbonate of soda. Carbonate of silver is thus formed, which readily dissolves in nitric acid. The silver may be precipitated from nitric acid by solution of common salt. Every 100 parts of the precipitate, washed, dried, and ignited, contain 75.5 of silver. But, as lead may be present in the solution, and this metal is also precipitated by common salt, it may be proper to immerse in the solution (which should not have any excess of acid) a polished plate of copper. This will precipitate the silver, if present, in a metallic form. The

chloride of silver is also soluble in liquid ammonia, which that of lead is not. For examples of the analysis of silver ores, the reader may consult Klaproth, vol. i. page 554, &c. and Bonsdorff, in the Ann. of Phil. N. S. viii. 29.

3. *Copper ores* may be analyzed by boiling them with five times their weight of concentrated sulphuric acid, mixed with one part of nitric acid, till a dry mass is obtained, from which water will extract the sulphate of copper. This salt is to be decomposed by a polished plate of iron, immersed in a dilute solution of it. The copper will be precipitated in a metallic state, and may be scraped off and weighed.

If silver be suspected along with copper, nitric acid only must be employed as the solvent; and a plate of polished copper will detect the silver.

The reader, who engages in the analysis of copper ores, will derive much advantage from the examples to be found in Klaproth's Essays, vol. i. pages 54, 541, &c.; and also from Mr. Chenevix's paper on the analysis of arseniates of copper and iron, Philosophical Transactions, 1801, or Nicholson's Journal, 8vo. vol. i.; from Vauquelin's remarks in Thomson's Annals, iv. 157; and from Mr. R. Phillips's Essays in the Quarterly Journal, iv. 274, and vii. 100, and in the Annals of Philosophy, N. S. iii. 81, 296.

4. *Iron ores* may be dissolved in diluted muriatic acid, or, if the metal be too highly oxidized to be dissolved by this acid, they must be previously mixed with one-eighth of their weight of powdered charcoal, and calcined in a crucible for one hour. The iron is thus rendered soluble.

The solution must then be diluted with 10 or 12 times its quantity of water, previously well boiled, to expel the air, and must be preserved in a well-stopped glass bottle for six or eight days. The phosphate of iron will, within that time, be precipitated, if any be present, and the liquor must be decanted off.

The solution may contain the oxides of iron, manganese, and zinc. It may be precipitated by carbonate of soda, which will separate them all. The oxide of zinc will be taken up by a solution of pure ammonia; distilled vinegar will take up the manganese, and will leave the oxide of iron; or the two last oxides may be separated as already directed page 591. From the weight of the oxide of iron, after ignition during a quarter

of an hour, 30 per cent. may be deducted. The remainder shows the quantity of metallic iron.

For an example of the analysis of an argillaceous iron ore *viâ humidâ*, the reader may consult the Ann. of Phil. N. S. vii. 448, and viii. 72. An excellent Metallurgical Memoir on this kind of iron ore, by Dr. Colquhoun, appeared in Dr. Brewster's Edinb. Journ. 1827. An example of the analysis of phosphate of iron, by Vauquelin, may be consulted in Ann. de Ch. et de Ph. xxx. 202.

5. *Tin ores.* To that accomplished analyst, Klaproth, we owe the discovery of a simple and effectual mode of analyzing tin ores in the humid way.

Boil 100 grains, in a silver vessel, with a solution of 600 grains of hydrate of potassa. Evaporate to dryness, and then ignite, moderately, for half an hour. Add boiling water, and, if any portion remain undissolved, let it undergo a similar treatment.

Saturate the alkaline solution with muriatic acid, which will throw down oxide of tin. Let this be re-dissolved by an excess of muriatic acid; again precipitated by carbonate of soda; and, being dried and weighed, let it, after lixiviation, be once more dissolved in muriatic acid. The insoluble part consists of silica. Into the colourless solution, diluted with two or three parts of water, put a stick of zinc, round which the reduced tin will collect. Scrape off the deposit, wash, dry, and fuse it under a cover of tallow in a capsule placed on charcoal. A button of pure metallic tin will remain at the bottom, the weight of which, deducted from that of the ore, indicates the proportion of oxygen.

The presence of tin in an ore is indicated by a purple precipitate, on mixing its solution in muriatic acid with one of gold in nitro-muriatic acid.

6. *Lead ores* may be analyzed by solution in nitric acid, diluted with an equal weight of water. The sulphur, if any, will remain undissolved. Let the solution be precipitated by carbonate of soda. If any silver be present, it will be taken up by pure liquid ammonia. Wash off the excess of ammonia by distilled water, and add concentrated sulphuric acid, applying heat, so that the muriatic acid may be wholly expelled. Weigh the calcined sulphate of lead, and for every 100 parts, 68 may be considered as lead.



Chloride of lead may be separated from chloride of silver by its greater solubility in warm water. From the solution, iron may be detached by ferro-cyanate of potassa, and the remaining liquid be decomposed by sulphuric acid. (See Vauquelin's Analysis of Galena, Journ. des Mines, No. 68; Klaproth's Analyses of Sulphate and Phosphate of Lead; Chenevix's Analysis of Native Muriate of Lead, Nicholson's Journal, 4to. vol. iv.; Hatchett on Bournonite (an ore of lead, antimony, and copper), Phil. Trans. 1804; Smithson on ditto, Phil. Trans. 1808, and Annals of Phil. xiv. 96; Vernon on Phosphate of Lead, Phil. Mag. and Ann. of Phil. i. 321.)

7. *Mercury* may be detected in ores that are supposed to contain it, by distilling them in an earthen retort with half their weight of iron filings or dry lime. The mercury, if any be present, will rise and be condensed in the receiver. See Klaproth's Analytical Essays.

8. *Ores of zinc* may be digested with nitric acid, and the part that is dissolved be boiled to dryness; again dissolved in the acid; and again evaporated. By this means the iron, if any be present, will be rendered insoluble in dilute nitric acid, which will take up the oxide of zinc. To this solution add pure liquid ammonia, in excess, which will separate the lead and iron, if any should have been dissolved, and the excess of alkali will retain the oxide of zinc. This may be precipitated by the addition of an acid, or by the evaporation of the solvent. Silica, also, is an abundant ingredient of some zinc ores. For examples of analyses of ores of zinc, see Smithson's Analysis of Calamine, Phil. Trans. 1803; Dr. Thomson's Analysis of Blende, Ann. of Phil. iv. 94; Berthier, in Silliman's American Journal, ii. 319; and Cooper, in Quarterly Journal, ix. 191.

9. *Antimonial ores.* Dissolve a given weight in three or four parts of muriatic and one of nitric acid. This will take up the antimony, and leave the sulphur, if any. On dilution with water, the oxide of antimony is precipitated, and the iron and mercury remain dissolved. Lead may be detected by sulphuric acid. (See Klaproth on the Analysis of Antimoniated Silver Ore, vol. i. p. 560, and Hatchett on Bournonite, Phil. Trans. 1804.)

10. *Ores of arsenic* may be digested with nitro-muriatic acid, composed of one part nitric, and one and a half or two parts of muriatic acid. Evaporate the solution to one-fourth, and add

water, which will precipitate the arsenic. The iron may afterwards be separated by ammonia. (See Chenevix, Philosophical Transactions, 1801, page 215; and Boussingault, Ann. de Ch. et de Ph. May, 1829, p. 75.)

11. *Ores of bismuth* may be assayed by digestion in nitric acid moderately diluted. The addition of water precipitates the oxide, as a sub-nitrate, but, if not wholly separated at first, evaporate the solution, after which a further addition of water will precipitate the remainder. (See Analysis of an Ore of Bismuth and Silver, in Klaproth, vol. i. page 554; Mode of detecting a small Quantity of Silver in Bismuth, Do. page 220, c.)

12. *Ores of cobalt* may be dissolved in nitro-muriatic acid. Then add carbonate of potassa, which at first separates iron and arsenic. Filter, and add a farther quantity of the carbonate, when a greyish red precipitate will fall down, which is oxide of cobalt. The iron and arsenic may be separated by heat, which volatilizes the arsenic. Cobalt is also ascertained, if the solution of an ore in muriatic acid give a sympathetic ink. (See chap. ix. sect. 27.—An example of the analysis of an ore of cobalt may be seen in Klaproth, vol. i. page 554; and of sulphate of cobalt, Do. page 579.)

13. *Ores of nickel*. Dissolve them in nitric acid, and add to the solution pure ammonia, in such proportion that the alkali may be considerably in excess. This will precipitate most other metals, and will retain the oxide of nickel in solution, which may be obtained by evaporation to dryness, and heating the dry mass till the nitrate of ammonia has sublimed. (See Berzelius on the Methods of analyzing Ores of Nickel, Ann. of Phil. N. S. iii. 206.)

14. *Ores of manganese*. The earths, and several of the metals contained in these ores, may first be separated by diluted nitric acid, which does not act on highly oxidized manganese. The ore may afterwards be digested with strong muriatic acid, which will take up the oxide of manganese. Chlorine gas will arise, if a gentle heat be applied, and may be known by its peculiar smell, and by its discharging the colour of wet litmus paper exposed to the fumes. From muriatic acid the manganese is precipitated by carbonate of soda, in the form of a white carbonate, which becomes black peroxide when heated in a crucible. Ores, suspected to contain manganese, may also be distilled *per se*, or with sulphuric acid, when oxygen gas will be obtained.

Oxide of manganese may be separated from oxide of iron by solution of pure potassa, which takes up the former, but not the latter. (See the analysis of an ore of manganese, *viâ humidâ*, in Klaproth, vol. i. p. 510; and of a cobaltic ore of manganese, page 569.)

Ores of manganese may also be distinguished by the colour they impart to borax, when exposed together to the blowpipe. (See chap. ix. sect. 14; and also Thomson's Annals, iii. 312.)

15. *Ores of uranium.*—These may be dissolved in dilute nitric acid, which takes up the oxide of uranium, and leaves that of iron; or in dilute sulphuric acid, which makes the same election; or, if any iron has got into the solution, it may be precipitated by zinc. Then add caustic potassa, which throws down the oxides of zinc and uranium. The former may be separated by digestion in pure ammonia, which leaves undissolved the oxide of uranium. This, when dissolved by dilute sulphuric acid, affords, on evaporation, crystals of a lemon yellow colour.

If copper be present, it will be dissolved, along with the zinc, by the ammonia. If lead, it will form, with sulphuric acid, a salt much less soluble than the sulphate of uranium, and which, on evaporation, will therefore separate first. (See Gregor in Annals of Philos. v. 281; Herschell, same work, N. S. iii. 99; and Phillips, Do. v. 57.)

16. *Ores of tungsten.*—For these the most proper treatment seems to be digestion in nitro-muriatic acid, which takes up the earths and other metals. The tungsten remains in the form of a yellow oxide, distinguishable by its becoming white on the addition of liquid ammonia, from the oxide of uranium. To reduce this oxide to tungsten, mix it with an equal weight of dried blood, heat the mixture to redness, press it into another crucible, which should be nearly full, and apply a violent heat for an hour at least. (See Klaproth's Analytical Essays; D'Elhuyar Mem. de l'Acad. de Toulouse, ii.; Vauquelin, Journ. des Mines, No. xix.; and Ann. de Ch. et de Ph. xxx. 194.)

17. *Ores of molybdenum.*—Repeated distillation to dryness, with nitric acid, converts the oxide of molybdenum into an acid, which is insoluble in nitric acid, and may thus be separated from other metals, except iron, from which it may be dissolved by sulphuric or muriatic acids. The solution in

sulphuric acid is blue, when cold, but colourless, when heated. That in muriatic acid is blue, only when the acid is heated and concentrated. (See Hatchett's Analysis of the Carinthian Molybdate of Lead, Philosophical Transactions, 1796; and Klaproth, vol. i. pp. 534, 538.)

Respecting the ores of the remaining metals, sufficient information has been already given for the purposes of the general student, and they are of such rare occurrence, that it is unnecessary to describe them more in detail. It may be proper, however, to state where the best examples of the analysis of each may be found.

18. *Ores of titanium*.—Consult Gregor, in Journ. de Physique, xxxix. 72, 152; Klaproth, i. 496; and Chenevix, Nicholson's Journal, v. 132.

19. *Ores of tellurium*.—See Klaproth, ii. 1.

20. *Ores of chromium*.—Vauquelin, Ann. de Chim. xxv.

21. *Ores of columbium*.—Hatchett, Phil. Trans. 1802; Ann. de Chimie, xliii. 276.

22. *Ores of palladium and rhodium*.—Wollaston, Phil. Trans. 1805, 1809, and 1829; Baruel, Quart. Journ. xii.; and Berzelius, Ann. de Ch. et de Ph. xl.

23. *Ores of iridium and osmium*.—Tennant, Phil. Trans. 1804; Baruel, Quart. Journ. xii. 247; Berzelius, Ann. de Ch. et de Ph. xl.

24. *Ores of cerium*.—Hisinger and Berzelius, and Vauquelin, Nicholson's Journ. 8vo. xii.

#### ART. 6.—*Analysis of Ores in the Dry Way.*

To analyze ores in the dry way, a method which affords the most satisfactory evidence of their composition, and should always precede the working of large quantities of ore, more elaborate processes and a more complicated apparatus are required.—An assaying furnace, with muffles, crucibles, &c., is absolutely necessary. These have already been enumerated in the chapter on Apparatus, and will be fully described in the Explanation of the Plates. Much useful information respecting the composition of minerals may also be gained from experiments with the blow-pipe. Ample directions for assays of this kind are given in a Memoir by Haussman, in the 43d volume of the Philosophical Magazine; by Gahn in the 11th volume of Dr. Thomson's Annals, p. 40; and by Berzelius, in a work

expressly devoted to the purpose, which has been lately translated, and published with valuable additions, by Mr. Children (1 vol. 8vo. London, 1822). To this work I refer the reader for a variety of details, which require attention in metallurgic experiments with the blow-pipe. In the Appendix, a table will be found, exhibiting the appearances of the different earths and metallic oxides under that instrument.

The reduction of an ore requires, frequently, previous roasting, to expel the sulphur and other volatile ingredients, which are replaced by oxygen derived from the atmosphere. The same end may be effected, by mixing the powdered ore with nitre, and projecting the mixture into a red-hot crucible. The sulphate of potassa, thus formed, may be washed off from the oxide, which must be reserved for subsequent experiments.

As many of the metals retain their oxygen so forcibly, that the application of heat is incapable of expelling it, the addition of inflammable matter becomes necessary. To enable the reduced particles of metal to agglutinate and form a collected mass, instead of scattered grains, which would be difficult to collect and to weigh, some fusible ingredient must be added, through which, when in fusion, the reduced metal may descend, and be collected in a mass at the bottom of the crucible. Substances that answer both these purposes are called *fluxes*. The alkaline and earthy part of fluxes serve also another end, *viz.*, that of combining with any acid which may be attached to a metal, and which would prevent its reduction, if not separated.

The ores of different metals, and different ores of the same metal, require different fluxes. To offer rules, however, for each individual case, would occupy too much room in this work: I shall, therefore, only state a few of those fluxes that are most generally applicable.

The *black flux* is formed, by setting fire to a mixture of one part of nitrate of potassa, and two of bi-tartrate of potassa; which affords an intimate mixture of sub-carbonate of potassa with a fine light coal. *White flux* is obtained by projecting into a red-hot crucible equal weights of the same salts. Two parts of common salt, previously dried in a crucible, one part of dry and powdered lime, one part of fluate of lime, and half a part of charcoal; or 400 parts of calcined borax, 40 of lime, and 50 of charcoal; or, two parts of pounded and finely sifted glass, one of borax, and half a part of charcoal, are all well adapted

to the purpose of fluxes. The ore, after being roasted, if necessary, is to be well mixed with three or four times its weight of the flux, and put into a crucible, with a little powdered charcoal over the surface. A cover must be luted on, and the crucible exposed to the necessary heat in a wind-furnace. Ores of iron being difficultly reduced, require a very intense fire. Those of silver and lead are metallized by a lower heat. The metal is found at the bottom of the crucible, in the form of a round button.

The volatile metals, as mercury, zinc, arsenic, tellurium, and osmium, it is obvious, ought not to be treated in the above manner, and require to be distilled with inflammable matters in an earthen retort.

For minute instructions respecting the analysis of every species of ore, both in the humid and dry ways, I refer to the second volume of Mr. Kirwan's Mineralogy, and to a Treatise on the General Principles of Chemical Analysis, translated from the French of Thenard, by Mr. Children, and to the work of Berzelius, de l'Analyse des Corps Inorganiques. Various excellent examples, which may be studied with great advantage, may be found in the essays of Vauquelin, dispersed through the Annales de Chimie; in those of Mr. Hatchett and Mr. Chenevix, in the Philosophical Transactions; of Dr. Kennedy, in Nicholson's Journal; and of Mr. Klaproth, in the work already frequently referred to. It is only, indeed, by an attention to these, and to other models of chemical skill and accuracy which are to be found in the various philosophical journals, conjoined with the practical imitation of them, that facility or certainty, in the difficult art of assaying, can be acquired; and though general rules are, in this instance, of considerable utility, it is impossible to frame any, that can be adapted to the infinite variety, which nature presents in the metallic products of the mineral kingdom.

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#### SECTION IV.

##### *On the Methods of discovering Poisons.*

When sudden death is suspected to have been occasioned by the administration of poison, either wilfully or by accident, the testimony of the physician is occasionally required to confirm or

invalidate this suspicion. He may also be sometimes called upon to ascertain the cause of the noxious effects arising from the presence of poisonous substances in articles of diet; and it may therefore serve an important purpose, to point out concisely the simplest and most practicable modes of obtaining, by experiment, the necessary information. Those persons, who wish to study the subject more at large, are referred to the Treatise on Poisons of M. Orfila, translated into English in 2 vols. 8vo., with an Appendix forming a third volume.

The poisons, that can be most clearly and decisively detected by chemical means, are those of the mineral kingdom; for vegetable poisons, though they may sometimes be identified by their taste, colour, or odour, are much less easily discriminated. Arsenic, and corrosive sublimate\* are most likely to be exhibited with the view of producing death; and lead and copper may be introduced undesignedly, in several ways, into our food and drink. The continued operation of the two last may often produce effects less sudden and violent, but not less baneful to health and life, than the more active poisons; and their operation being generally unsuspected, involves, in its pernicious consequences, a greater number of sufferers.

#### ART. I.—*Method of discovering Arsenic.*

When the cause of sudden death is believed, from the symptoms preceding it, to be the administration of arsenic (arsenious acid), the contents of the stomach must be attentively examined. To effect this, let a ligature be made at each orifice, the stomach removed entirely from the body, and its whole contents washed out into an earthen or glass vessel. The arsenic on account of its greater specific gravity, will settle to the bottom, and may be obtained separate, after washing off the other substances by repeated affusions of cold water. These washings should not be thrown away, till the presence of arsenic has been clearly ascertained. It may be expected at the bottom of the vessel in the form of a white powder, which must be carefully collected, dried on a filter, and submitted to experiment.

When a substance of this kind, differing from the ordinary contents of the stomach, can be thus distinctly exhibited, the

\* By the name *arsenic*, used in a popular sense, the *arsenious acid*, described p. 53, is meant; and by *corrosive sublimate*, the *bichloride of mercury*, p. 135.

evidence of its nature is supplied by very easy and satisfactory processes. The shortest and most conclusive is, the reduction of the arsenious acid to the metallic state, in which the characters of arsenic are clear and unequivocal, and, if developed, leave no doubt as to the cause of death. The experiment requires only a very simple apparatus, and no more skill than is easily attained by a person attentive to the following directions, even though he may not be in the habit of chemical manipulation. It will be necessary, in the first place, to procure a glass tube from  $\frac{1}{7}$  to  $\frac{1}{10}$ th of an inch diameter, and five or six inches long. Berzelius recommends that it be drawn out at one end into a still narrower tube, of such diameter, for the extent of about 2 or 3 inches, as barely to admit a coarse knitting needle, thus :



The form, however, is not essential, and a tube of equal diameter throughout will sufficiently answer the purpose.

A small portion of the substance suspected to contain arsenic (one hundredth of a grain has been found enough) previously dried, is to be pushed by a knitting needle to the end *a*, and then covered with perfectly dry charcoal powder or *black flux* (see p. 609) as far as *b*. The tube is then to be held horizontally, and the part *b* to be placed in the flame of a small spirit lamp, keeping the part *a* out of the flame till the charcoal is heated to redness, when the end *a* is to be brought into the flame. The arsenious acid is now volatilized; and, during its passage through the ignited charcoal, is reduced. The metallic arsenic is condensed, and forms a brilliant coating, on that part of the inner surface of the small end of the tube which has not been heated. By heating the place where it is deposited, the metal may be driven farther on; and, by applying heat as before, a further portion will probably be condensed in the same place. The tube may next be cut by a file between the charcoal and the metal. On heating the latter, a distinct smell of garlic will be perceived, a character peculiar to arsenic among the metals, but not possessed by its oxide. We may, also, re-convert the metal into arsenious acid, by exposing that part of the tube, to which it adheres, within three quarters of an inch above the flame of a spirit lamp. The metal is oxidized, and the regenerated arsenious acid rises



into the cool part of the tube, and is deposited in crystals, easily recognized by a practised eye. It is necessary, however, that the inside of the tube should be quite clean and dry. These characters sufficiently identify arsenic; but if thought necessary, a small fragment of the metal detached by a knife from the tube may be placed, surrounded by a little charcoal, between two thin plates of polished copper, from half an inch to an inch square, which may be bound together by iron wire. On heating these to low redness, and then separating them, the copper surfaces will be found to have acquired a white spot or stain.

It is not in all cases that arsenic, sufficient for actual reduction, can be obtained in a separate form; for it is possible that it may have either been administered in solution, or that it may have been dissolved by the fluids present in the stomach. In this case its discovery is more difficult; but there are two methods by which evidence of its presence may be obtained. The first consists in adding, to the filtered contents of the stomach, some substance which has an affinity for arsenious acid, and which is capable of throwing it down in the state of an insoluble compound. Lime water has this property; and, from a solution of arsenious acid, precipitates an insoluble arsenite of lime, which may be collected by washing off the other matter, and then dried. This may be treated for arsenic in the manner already directed. Or, through the clear liquor, obtained by filtering the contents of the stomach, we may pass a current of sulphureted hydrogen gas. This will throw down a yellow sulphuret of arsenic (orpiment), from which metallic arsenic may be obtained by the tube process; but in this case, as well as in the last, the black flux is decidedly preferable to charcoal, on account of the potassa which it contains.

Berzelius, in order to decompose the sulphuret of arsenic, mixes it with carbonate of soda in excess, and moistens the mixture with a little water. He then, by means of a very thin rod of glass, introduces it into the wider part of the tube represented above, which, for this purpose, is left open at both ends. Having placed it within an inch from the contracted part, the tube is heated, in order to melt the mixture, and while fused, hydrogen gas deprived of moisture is passed over it, the heat being increased, towards the close of the process, by the blow-pipe. The arsenic is reduced by the hydrogen, and is deposited in the cool part of the tube. (*Ann. de Ch. et de Ph. Sep. 1828.*)

Liebig prefers transmitting the sulphuret in vapour over the ignited black powder, left by calcining tartrate of lime. (Quart. Journ. July, 1829.)

*Tests of arsenic.*—It has been usual to rely much upon tests of the presence of arsenious acid, that is, upon liquids which denote its presence by the colours which they produce with its solutions. When, from any cause, we do not succeed in obtaining metallized arsenic, these tests may have their value; and they may be called in aid when the smallest doubt exists of the evidence afforded by the reduction of the metal. Their application, indeed, is attended with very little trouble, and though, singly, they cannot be trusted, yet if they all concur in establishing the same point, they may certainly be considered as strongly confirming any circumstantial evidence, derived from testimony, of the exhibition of arsenic. In the investigation, too, of so serious a charge as that of murder, justice to the accused and to the community equally demand that no source of chemical demonstration should be left unexplored. For these reasons, I shall give a more minute history of the action of tests, than would otherwise have been advisable.

The liquid, submitted to experiment, may be either the fluid found in the stomach, cleared by filtration through paper, or a solution of any powder which may be found in that organ.

(A) *Sulphureted hydrogen test.*—Add to the solution a portion of water, saturated with sulphureted hydrogen gas; or, as Mr. Philips recommends, (Ann. of Phil. N. S. vii. 32,) pass the gas through the liquid. For this purpose, put into a clean Florence oil flask about two ounces of strong muriatic acid, and an ounce and a half of powdered sulphuret of antimony. The gas may be conducted into the solution by a glass tube or tin pipe twice bent at a right angle. If arsenic be present, a golden yellow sediment will fall down, which will appear sooner, if a few drops of acetic acid be added.

A similar effect is produced by the addition of sulphuret of ammonia, or hydro-sulphuret of potassa.

It is necessary, however, to observe that these tests are decomposed, not only by all metallic solutions, but by the mere addition of any acid. But among these precipitates, Dr. Bostock assures us, (Edinburgh Medical and Surgical Journal, v. 166,) the greatest part are so obviously different, as not to afford a probability of being mistaken; the only two, which bear a

close resemblance to sulphuret of arsenic, are the precipitate from tartarized antimony, and that separated by an acid. In the latter, however, the sulphur preserves its peculiar yellow colour, while the arsenical sulphuret presents a deep shade of orange; but no obvious mark of discrimination can be pointed out between the hydro-sulphurets of arsenic and of antimony; and recourse must, therefore, be had to the process of reduction by the black flux.

(B) *Scheele's Green*.—To a little of the suspected fluid, add a single drop of a weak solution of subcarbonate of potassa, and afterwards a few drops of a solution of sulphate of copper, which should, for this purpose, be quite free from iron. The presence of arsenic will, under circumstances favourable to the result, be manifested by a yellowish green precipitate. Or a portion of a suspected powder may be boiled with a dilute solution of pure potassa, and a few drops of sulphate of copper be added, when a similar appearance will ensue still more remarkably, if arsenic be present. The colour of this precipitate is perfectly characteristic. It is that of the pigment called Scheele's green. But the test is a fallacious one, because, as Dr. Christison has shown, it produces a greenish precipitate from some animal and vegetable infusions which contain no arsenic; and fails to give the characteristic appearances in other mixed fluids, as in tea and porter, to which arsenic has been purposely added. In the latter case, Mr. R. Phillips destroys the colour of the fluid, by previously digesting it with animal charcoal (ivory black) and then filtering it. This renders it so transparent, that the most delicate tests of arsenious acid become effectual. But as animal charcoal contains a little common salt, which would interfere with the test (c), the charcoal must be previously washed with distilled water.

The proportions, in which the different ingredients are employed, when we operate on a colourless solution of arsenic, Dr. Bostock has found to have considerable influence on the distinct exhibition of the effect. Those, which he observed to answer best, were one of arsenic, three of potassa, and five of sulphate of copper. For instance, a solution of one grain of arsenic and three grains of potassa, in two drachms of water, being mingled with another solution of five grains of sulphate of copper in the same quantity of water, the whole was converted into a beautiful grass green, from which a copious precipitate of the same hue slowly subsided, leaving the superna-

tant liquor transparent and nearly colourless. Sulphate of copper only, without arsenic, being employed in the same manner, a delicate sky-blue resulted, so different from the former, as not to admit of the possibility of mistake. In this way,  $\frac{1}{40}$ th of a grain of arsenic, diffused through sixty grains of water, afforded, by the addition of sulphate of copper and potassa in proper proportions, a decided precipitate of Scheele's green. In employing this test, it is necessary to view the fluid by reflected and not by transmitted light, and to make the examination by day-light. To render the effect more apparent, a sheet of white paper may be placed behind the glass in which the mixed fluids are contained; or the precipitation may be effected by mixing the fluids on a piece of writing paper.

(C) *Ammonia-nitrate of Silver*.—A process for detecting arsenic was proposed by Mr. Hume, of London, in the *Philosophical Magazine* for May, 1809, vol. xxxiii. The test, which he suggested, is the fused nitrate of silver or lunar caustic, employed in the following manner: (Lond. Med. and Phys. Journ. xxiii. 448.)

Into a clean Florence oil flask, introduce two or three grains of any powder suspected to be arsenic; add not less than eight ounce-measures of either rain or distilled water; and heat this gradually over a lamp or clear coal fire, till the solution begins to boil. Then, while it boils, frequently shake the flask, which may be readily done by wrapping a piece of leather round its neck, or putting a glove upon the hand. To the hot solution, add a grain or two of sub-carbonate of potassa or soda, agitating the whole to make the mixture uniform

In the next place, pour into an ounce phial or a small wine glass about two table spoonfuls of the cooled solution, and present, to the mere surface of the fluid, a stick of dry nitrate of silver or lunar caustic. If there be any arsenic present, a beautiful yellow precipitate will instantly appear, which will proceed from the point of contact of the nitrate with the fluid; and settle towards the bottom of the vessel as a flocculent and copious precipitate.

The nitrate of silver, Mr. Hume found, acts also very sensibly upon *arsenate* of potassa, and decidedly distinguishes this salt from the above solution or *arsenite* of potassa; the colour of the precipitate, occasioned by the *arsenate*, being much darker and more inclined to brick-red. In both cases, he

is of opinion that the test of nitrate of silver is greatly superior to that of sulphate of copper; inasmuch as it produces a much more copious precipitate, when equal quantities are submitted to experiment. The tests he recommends to be employed in their dry state, in preference to that of solution; and that the piece of lunar caustic be held on the surface only.

A modified application of this test was afterwards proposed by Dr. Marcet, whose directions are as follows: let the fluid, suspected to contain arsenic, be filtered; let the end of a glass rod, wetted with a solution of pure ammonia, be brought into contact with this fluid, and let the end of a clean rod, similarly wetted with solution of nitrate of silver, be immersed in the mixture. If the minutest quantity of arsenic be present, a precipitate of a bright yellow colour inclining to orange will appear at the point of contact, and will readily subside to the bottom of the vessel. As this precipitate is soluble in ammonia, the greatest care is necessary not to add an excess of that alkali. The acid of arsenic, with the same test, affords a brick-red precipitate. (*Med. Chir. Trans.* ii. 156.) Mr. Hume conceived that the silver test is rendered still more certain, by dissolving a few grains, say ten, of lunar caustic in nine or ten times its weight of distilled water; precipitating by liquid ammonia; and adding cautiously, and by a few drops at once, liquid ammonia, till the precipitate is redissolved, and no longer. To obviate the possibility of any excess of ammonia, a small quantity of the precipitate may even be left undissolved. To apply this test, nothing more is required than to dip a rod of glass into this liquor, and then to touch with it the surface of a solution supposed to contain arsenic, which will be indicated by a yellow precipitate.

The late Mr. Sylvester objected to this test, that it will not produce the expected appearance, when common salt is present. He, therefore, proposed the red acetate of iron as a better test of arsenic, with which it forms a bright yellow deposit; or the acetate of copper, which affords a green precipitate. Of the two, he recommended the latter in preference, but advised that both should be resorted to in doubtful cases. (*33 Nich. Journ.* 306.) Dr. Marcet, however, ascertained, that the objection arising from the presence of common salt is easily obviated; for if a little diluted nitric acid be added to the suspected liquid, and then nitrate of silver be very cautiously poured in, till the

precipitate ceases, the muriatic acid will be removed, but the arsenic will remain in solution, and the addition of ammonia will produce the yellow precipitate in its characteristic form. It is scarcely necessary to add that the quantity of ammonia must be sufficient to saturate any excess of nitric acid which the fluid may contain. (Phil. Mag. xli. 124.)

A more important objection to nitrate of silver as a test of arsenic is, that it affords, with the alkaline phosphates, a precipitate of phosphate of silver, scarcely distinguishable by its colour from the arseniate of that metal. (Thomson's Annals, viii. 152.) In answer to this, it is alleged by Mr. Hume, that the arsenite of silver may be discriminated by a curdy or flocculent figure, resembling that of fresh precipitated muriate of silver, except that its colour is yellow; while the phosphate is smooth and homogeneous. (Med. and Phys. Journ. Jan. 1818.) The better to discriminate these two arsenites, he advises two parallel experiments to be made, upon separate pieces of clean writing paper, spreading on the one a little of the fresh prepared arsenite, and on the other a little of the phosphate. When these are suffered to dry, the phosphate will gradually assume a black colour, or nearly so, while the arsenite will pass from its original vivid yellow to an Indian yellow, or nearly a fawn colour.

Dr. Paris conducts the trial by the silver test in the following manner: drop the suspected fluid on a piece of white paper, making with it a broad line; along this line a stick of lunar caustic is to be slowly drawn several times successively, when a streak will appear of the colour resembling that known by the name of *Indian yellow*. This is equally produced by arsenic and by an alkaline phosphate; but the one from arsenic is rough, curdy, and flocculent, like that from a crayon; that from a phosphate is homogeneous and uniform, resembling a water colour laid smoothly on with a brush. But a more important and distinctive peculiarity soon succeeds; for in less than two minutes the phosphoric yellow fades into a *sad green*, and becomes gradually darker, and ultimately quite black, while on the other hand the arsenic yellow continues permanent, or nearly so, for some time, and then becomes brown. In performing this experiment, the sunshine should be avoided, or the change of colour will take place too rapidly. (Ann. of Phil. x. 60.) The author of the London Dispensary adds, that the test is

improved by brushing the streak lightly over with liquid ammonia immediately after the application of the caustic, when, if arsenic be present, a bright queen's yellow is produced, which remains permanent for nearly an hour; but that when lunar caustic produces a *white* yellow before the ammonia is applied, we may infer the presence of some alkaline phosphate rather than of arsenic.

(D) *Conversion of the arsenious into arsenic acid.*—Mr. Smithson proposes to fuse any powder suspected to contain arsenic with nitre; this produces arseniate of potassa, of which the solution affords a brick-red precipitate with nitrate of silver. In cases where any sensible portion of the alkali of the nitre has been set free, it must be saturated with acetous acid, and the saline mixture dried and re-dissolved in water. So small is the quantity of arsenic required for this mode of trial, that a drop of solution of oxide of arsenic in water (which at 54° Fahr. may be estimated to contain  $\frac{1}{80}$ th its weight of the oxide), mixed with a little nitrate of potassa, and fused in a platinum spoon, affords a very sensible quantity of arseniate of silver. (Ann. of Phil. N. S. iv. 127.)

(E) *Chromates.*—Dr. Cooper, President of Columbia College, finds a solution of chromate of potassa to be one of the best tests of arsenic. One drop is turned green by the fourth of a grain of arsenic, by two or three drops of Fowler's mineral solution, or any other arsenite of potassa. The arsenious acid takes oxygen from the chromic, which is converted into green oxide of chrome. To exhibit the effect, take five watch glasses; put on one, two or three drops of a watery solution of white arsenic; on the second, as much arsenite of potassa; on the third, one fourth of a grain of white arsenic in substance; on the fourth, two or three drops of solution of corrosive sublimate; on the fifth, two or three drops of a solution of copper. Add to each three or four drops of a solution of chromate of potassa. In half an hour a bright clear grass green colour will appear in numbers 1, 2, 3, unchangeable by ammonia: number 4 will instantly exhibit an orange precipitate; and number 5 a green, which a drop of ammonia will instantly change to blue. (Silliman's American Journal, iii.)

The experiments, which have been described, are adapted to discover arsenic when dissolved in a watery fluid. If the solvent be oil, or if much oil be present, a different course be-

comes necessary. In this case, Dr. Ure proposes to boil and agitate the oily liquid with distilled water, and afterwards to separate the oil by the capillary action of wick threads. The watery fluid may then be subjected to the usual tests.

ART. II. *Discovery of Hydro-cyanic (Prussic) Acid, Opium, and Morphia.*

1. *Hydro-cyanic Acid.*—This acid may be recognized by the characters described vol. i. p. 478, as well as by its strong flavour of bitter almonds. M. M. Lassaigne and Leuret, however, have found that hydrocyanic acid cannot be discovered in animals that have been killed by small doses of it, if the bodies are previously exposed to the air for two or three days; that after a longer time than this, the poison undergoes decomposition, which is favoured by the presence of putrescent animal matter: and they state that when it is requisite to examine a body, with the view of ascertaining the presence of this poison, it should be done as soon as possible after death. (Phil. Mag. and Ann. of Phil. Sep. 1827.)

2. *Opium.*—Dr. Hare of Philadelphia has contrived a method by which a quantity of opium, not exceeding that contained in ten drops of laudanum, may be detected in half a gallon of water. The process is founded on the property, which meconic acid has of precipitating with lead. Hence, by adding a few drops of acetate of lead to any infusion containing opium, in not less than the above proportion, an observable quantity of meconate of lead falls down. The precipitation, where the quantity is small, may require from six to eight hours, and may be facilitated by very gentle stirring with a glass rod, to detach the flocks from the sides of the glass vessel, which should be conical, so as to concentrate them during their descent. The meconate of lead being thus collected at the bottom of the vessel, let about thirty drops of sulphuric acid be poured upon it through a glass tube. Let this be followed by about as much of the red sulphate of iron. The sulphuric acid liberates the meconic, and enables it to produce, with the iron, the appropriate red colour which demonstrates the presence of that acid, and consequently of opium. (Same work, p. 233.)

3. *Morphia.*—M. Lassaigne filtered the contents of the stomach of an animal poisoned by acetate of morphia, evaporated the fluid carefully, and treated the dry mass with boiling alcohol,



sp. gr. .837. The alcoholic solution was evaporated to the consistence of an extract, and treated with distilled water, to separate the fatty matter; the solution, then filtered, deposited by gentle evaporation prismatic crystals at the bottom of the capsule, which had the following properties, belonging to acetate of morphia: they had a bitter taste, and were precipitated in white flakes from this solution in water by ammonia; treated with concentrated sulphuric acid in a small glass tube closed at one end, they exhaled a decided odour of acetic acid; they immediately gave a yellow solution with nitric acid, which, with an increased quantity of acid, deepened to orange, and afterwards exhibited a fine blood colour. (Ann. of Phil. N. S. viii. 283.)

ART. III.—*Discovery of Corrosive Sublimate, Baryta, &c.*

Corrosive sublimate (the bi-chloride or oxy-muriate of mercury), next to arsenic, is the most virulent of the metallic poisons. It may be collected by treating the contents of the stomach in the manner already described; but as it is more soluble than arsenic, *viz.* in about 19 times its weight of water, no more water must be employed than is barely sufficient, and the washings must be carefully preserved for examination.

If a powder should be collected, by this operation, which proves, on examination, not to be arsenic, it may be known to be corrosive sublimate by the following characters :

(A) Expose a small quantity of it, without any admixture, to heat in a coated glass tube, as directed in the treatment of arsenic. Corrosive sublimate will be ascertained by its rising to the top of the tube, lining the inner surface in the form of a shining white crust.

(B) Dissolve another portion in distilled water; and it may be proper to observe how much of the salt the water is capable of taking up.

(C) To the watery solution add a little lime-water. A precipitate of an orange yellow colour will instantly appear.

(D) To another portion of the solution add a single drop of a dilute solution of sub-carbonate of potassa (salt of tartar). A white precipitate will appear; but, on a still farther addition of alkali, an orange-coloured sediment will be formed.

(E) The carbonate of soda has similar effects.

(F) Sulphureted water throws down a dark-coloured sediment, which, when dried and strongly heated, is wholly volatilized, without any odour of garlic.

For the detection of corrosive sublimate, Mr. Sylvester has recommended the application of galvanism, which exhibits the mercury in the metallic state. A piece of zinc wire, or, if that cannot be had, of iron wire, about three inches long, is to be twice bent at right angles so as to resemble the Greek letter  $\Pi$ . The two legs of this figure should be distant about the diameter of a common gold wedding-ring from each other, and the two ends of the bent wire must afterwards be tied to a ring of this description. Let a plate of glass, not less than three inches square, be laid as nearly horizontal as possible, and on one side drop some sulphuric acid, diluted with about six times its weight of water, till it spreads to the size of a halfpenny. Next at a little distance from this, towards the other side, drop some of the solution supposed to contain corrosive sublimate, till the edges of the two liquids join together; and let the wire and ring prepared as above be laid in such a way that the wire may touch the acid, while the gold ring is in contact with the suspected liquid. If the minutest quantity of corrosive sublimate be present, the ring in a few minutes will be covered with mercury on the part which touched the fluid.

Mr. Smithson remarks, that all the oxides and saline compounds of mercury, if laid in a drop of marine acid on gold, with a bit of tin, quickly amalgamate the gold. In this way, a very minute quantity of corrosive sublimate, or a drop of its solution, may be tried, and the addition of muriatic acid is not then required. Quantities of mercury may, by this little galvanic arrangement, be rendered evident, which could not be so by any other means. Even the mercury of cinnabar may be exhibited; but it must previously be boiled with a little sulphuric acid in a platinum spoon, to convert it into sulphate. An exceedingly minute quantity of metallic mercury in any powder may be discovered by placing it in nitric acid on gold, drying, and adding muriatic acid and tin. It is proper, however, not to dismiss this subject without stating, that M. Orfila has pointed out sources of fallacy in this test, which might lead to false conclusions; for he finds that gold is stained in the same manner, by a liquid totally free from mercury, provided it contain a little free acid or muriate of soda. In this case, a little proto-muriate of tin is formed, from which tin is precipitated upon the surface of the gold; and this stain is removed by heat, equally with the mercurial one. A drop of pure muriatic acid, however, discriminates the tin stain by

instantly removing it; but does not act in the same way on a stain produced by mercury. The latter volatile metal may be also exhibited by heating the whitened gold in a small glass tube, in the cold part of which globules of mercury, very minute, but still visible by a magnifier, will be condensed. (Ann. de Ch. et de Ph. May, 1829.)

The only mineral poison of great virulence that has not been mentioned, and which, from its being little known to act as such, it is very improbable we should meet with, is the carbonate of baryta. This, in the country where it is found, is employed as a poison for rats, and there can be no doubt that it would be equally destructive to human life. It may be discovered by dissolving it in muriatic acid, and by the insolubility of the precipitate which this solution yields on adding sulphuric acid, or sulphate of soda. Soluble barytic salts, if these have been the means of poison, will be contained in the water employed to wash the contents of the stomach, and will be detected on adding sulphuric acid, by a copious precipitation.

It may be proper to observe, that the failure of attempts to discover poisonous substances in the alimentary canal after death, is by no means a sufficient proof that death has not been occasioned by poison. For it has been clearly established, by experiments made on animals, that a poison may be so completely evacuated, that no traces of it shall be found, and yet that death may ensue from the morbid changes which it has occasioned in the alimentary canal, or in the general system.

#### ART. IV.—*Method of detecting Copper or Lead.*

Copper and lead sometimes gain admission into articles of food, in consequence of the employment of kitchen utensils of these materials.

I. If COPPER be suspected in any liquor, its presence will be ascertained by adding a solution of pure ammonia, which will strike a beautiful blue colour. If the solution be very dilute, it may be concentrated by evaporation; and if the liquor contain a considerable excess of acid, like that used to preserve pickles, as much of the alkali must be added as is more than sufficient to saturate the acid. In this, and all other experiments of the same kind, the fluid should be viewed by reflected, and not by transmitted, light.

If into a newly prepared tincture of guaiacum wood we drop

a concentrated solution of a salt of copper, the mixture instantly assumes a blue colour. This effect does not take place when the solution is very weak, for example, when there is not above half a grain of the salt to an ounce of water; but then, by the addition of a few drops of prussic acid, the blue colour is instantly developed of great purity and intensity. This colour is not permanent, but soon passes to a green, and at length totally disappears. For want of prussic acid, distilled laurel water may be employed. The test produces its effect, even when the proportion of the salt of copper to the water does not exceed 1-45000th. Of this minute proportion, no other test, whether the prussiate of potassa, soda, or ammonia, gives the least indication. (Quart. Journ. x. 182.)

II. LEAD is occasionally found, in sufficient quantity to be injurious to health, in water that has passed through leaden pipes or been kept in leaden vessels, and sometimes even in pump-water, in consequence of that metal having been used in the construction of the pump. Acetate of lead has also been known to be fraudulently added to bad wines, with the view of concealing their defects.

Lead may be discovered by adding, to a portion of the suspected water, about half its bulk of water impregnated with sulphureted hydrogen gas. If lead be present, it will be manifested by a dark brown, or blackish tinge. This test is so delicate, that water condensed by the leaden worm of a still-tub, is sensibly affected by it. Lead is also detected by a similar effect ensuing on the addition of sulphuret of ammonia, or potassa.

The accuracy, however, of this method of discovering very minute quantities of lead has been set aside by the experiments of Dr. Lambe,\* the author of a skilful analysis of the springs of Leamington Priors, near Warwick. By new methods of examination, he has detected the presence of lead in several spring-waters, that manifest no change on the addition of the sulphureted test; and has found that metal in the precipitate, separated from such waters by the carbonate of potassa or of soda. In operating on these waters, Dr. Lambe noticed the following appearances:

(a) The test forms sometimes a dark cloud, with the precipi-

\* See his "Researches into the Properties of Spring Water." 8vo. London. Johnson, 1803.

tate effected by alkalis, which has been re-dissolved in nitric acid.

(b) Though it forms, in other cases, no cloud, the precipitate itself becomes darkened by the sulphureted test.

(c) The test forms a white cloud, treated with the precipitate as in (a). These two appearances may be united.

(d) The test neither forms a cloud, nor darkens the precipitate.

(e) In the cases (b), (c), (d), heat the precipitate, in contact with an alkaline carbonate, to redness; dissolve out the carbonate by water; and treat the precipitate as in (a). The sulphureted test then forms a dark cloud with the solution of the precipitate. In these experiments, it is essential that the acid, used to re-dissolve the precipitate, shall not be in excess; and if it should so happen, that excess must be saturated before the test is applied. It is better to use so little acid, that some of the precipitate may remain undissolved.

(f) Instead of the process (e) the precipitate may be exposed without addition to a red heat, and then treated as in (a). In this case, the test will detect the metallic matter; but with less certainty than the foregoing one.

The nitric acid, used in these experiments, should be perfectly pure; and the test should be recently prepared by saturating water with sulphureted hydrogen gas. A few drops of nitric acid added to a water containing lead, which has been reduced to 1-8th or 1-10th its bulk by evaporation, and then followed by the addition of a few drops of hydriodate of potassa, produces a yellow insoluble precipitate.

Another mode of analysis, employed by Dr. Lambe, consists in precipitating the lead by solution of common salt; but as muriate of lead is partly soluble in water, this test cannot be applied to small portions of suspected water. The precipitate must be, therefore, collected, from two or three gallons, and heated to redness with twice its weight of carbonate of soda. Dissolve out the soda; add nitric acid, saturating any superfluity; and then apply the sulphureted test. Sulphate of soda would be found more effectual in this process than the muriate, on account of the greater insolubility of sulphate of lead. This property, indeed, renders sulphate of soda an excellent test of the presence of lead, when held in solution by acids, for it throws down that metal, even when present in very small quantity, in

the form of a heavy white precipitate, which is not soluble by acetic acid.

The third process, which is the most satisfactory of all, and is very easy, except for the trouble of collecting a large quantity of precipitate, is the actual reduction of the metal, and its exhibition in a separate form. The precipitate may be mixed with its own weight of alkaline carbonate, and exposed either with or without the addition of a small proportion of charcoal, to a heat sufficient to melt the alkali. On breaking the crucible, a small globule of lead will be found reduced at the bottom; or the reduction may be effected by the use of the blow-pipe. The precipitate from about fifty gallons of water yielded Dr. Lambe, in one instance, about two grains of lead.

For discovering the presence of lead in wines, a test invented by Dr. Hahnemann, and known by the title of Hahnemann's wine-test, may be employed. This test is prepared by putting together, into a small phial, sixteen grains of sulphuret of lime, prepared in the dry way (by exposing to a red heat, in a covered crucible, equal weights of powdered lime and sulphur, accurately mixed), and 20 grains of bitartrate of potassa (cream of tartar). The phial is to be filled with water, well corked, and occasionally shaken for the space of ten minutes. When the powder has subsided, decant the clear liquor, and preserve it, in a well-stopped bottle, for use. The liquor, when fresh prepared, discovers lead by a dark-coloured precipitate. A farther proof of the presence of lead in wines is the occurrence of a precipitate on adding a solution of the sulphate of soda.

Mr. Sylvester has proposed the gallic acid as an excellent test of the presence of lead. (33 Nicholson's Journal, 310.)

The quantity of lead, which has been detected in sophisticated wine, may be estimated at forty grains of the metal in every fifty gallons. (Lambe, page 175.)

When a considerable quantity of acetate of lead has been taken into the stomach (as sometimes, owing to its sweet taste, happens to children), after the exhibition of an active emetic, the hydro-sulphuret of potassa or of ammonia may be given; or probably a solution of sulphate of soda (Glauber's Salt) would render it innocuous.

# APPENDIX,

CONSISTING OF

## VARIOUS USEFUL TABLES.

CORRESPONDENCE BETWEEN ENGLISH AND FOREIGN  
WEIGHTS AND MEASURES.\*

### I.—*English Weights and Measures.*

#### Troy Weight.

Pound.	Ounces.	Drms.	Scruples.	Grains.
1	= 12	= 96	= 288	= 5760
	1	= 8	= 24	= 480
		1	= 3	= 60
			1	= 20
				1

#### Avoirdupois Weight.

Pound.	Ounces.	Drms.	Grains.
1	= 16	= 256	= 7000.
	1	= 16	= 437.5
		1	= 27.34375

#### Measures.

Gal.	Pints.	Ounces.	Drms.	Cub. Inch.
1	= 8	= 128	= 1024	= 231.
	1	= 16	= 128	= 28.875
		1	= 8	= 1.8047
			1	= 0.2256

N. B.—The English ale-gallon contains 282 cubical inches; or rather, according to the report of the Commissioners appointed to consider the subject of weights and measures, 277.3

\* For the most complete and authentic account of the correspondence between English and foreign weights and measures, the reader is referred to the last edition of Dr. Kelly's *Universal Cambist*.





4 To reduce the Swedish kannes to English wine pints, multiply by .1520207, or divide by 6.57805.

5. To reduce Swedish kannes to English wine gallons, multiply by .82225, or divide by 1.216.

6. The lod, a weight sometimes used by Bergman, is the 32d part of the common Swedish pound of 16 oz. and the 24th part of the pound of 12 oz. Therefore to reduce it to the English troy pound, multiply by .03557, or divide by 28.1156.

V.—*Correspondence of English Weights and Measures with those used in France previously to 1795.*

This Table of measures, which are now generally disused in France, is retained, because constant reference to it is necessary in reading the works of the French chemists, anterior to that period.

§ I.—WEIGHTS.

The Paris pound, *poids de marc* of Charlemagne, contains 9216 Paris grains; it is divided into 16 ounces, each ounce into 8 gros, and each gros into 72 grains. It is equal to 7561 English troy grains.

The English troy pound of 12 ounces contains 5760 English troy grains, and is equal to 7021 Paris grains.

The English avoirdupois pound of 16 ounces contains 7000 English troy grains, and is equal to 8532.5 Paris grains.

To reduce Paris grains to English troy grains,	}	1.2189
divide by .....		
To reduce English troy grains to Paris grains,	}	1.015734
multiply by .....		
To reduce Paris ounces to English troy, divide	}	1.015734
by .....		
To reduce English troy ounces to Paris, mul-	}	1.015734
tiply by .....		

Or the conversion may be made by means of the following tables:

1.—*To reduce French to English Troy Weight.*

The Paris pound	=	7561.	}	English troy grains.
The ounce	=	472.5625		
The gros	=	59.0703		
The grain	=	.8204		

2.—*To reduce English Troy to Paris Weight.*

The English troy pound of	}	= 7021.	} Paris grains.
12 ounces . . . . .			
The troy ounce . . . . .	= 585.0833		
The dram of 60 grains . . . .	= 73.1354		
The penny weight or denier	}	= 29.2541	
of 24 grains . . . . .			
The scruple of 20 grains . . . .	= 24.3784		
The grain . . . . .	= 1.2189		

3.—*To reduce English Avoirdupois to Paris Weight.*

The avoirdupois pound of 16	}	= 8538.	} Paris grains.
ounces, or 7000 troy grains			
The ounce . . . . .	= 533.6250		

§ II.—LONG AND CUBICAL MEASURES.

To reduce Paris running feet, or inches, into	}	1.065977
English, multiply by . . . . .		
English running feet, or inches, into Paris,	}	1.211278
divide by . . . . .		
To reduce Paris cubic feet, or inches, to Eng-	}	1.211278
lish, multiply by . . . . .		
English cubic feet, or inches, to Paris, divide	}	1.211278
by . . . . .		

Or by means of the following tables :

4.—*To reduce Paris Long Measure to English.*

The French toise = 6.3945 English feet.	
The Paris royal foot of 12 inches = 12.7977	} English inches.
The inch* . . . . . = 1.0664	
The line, or 1-12th of an inch . . = .0888	
The 1-12th of a line . . . . . = .0074	

5.—*To reduce English Long Measure to French.*

The English foot . . . . . = 11.2596	} Paris inches.
The inch . . . . . = .9383	
The 1-8th of an inch . . . . . = .1173	
The 1-10th . . . . . = .0938	
The 1-13th . . . . . = .0782	

\* Fifteen French inches, or feet, are very nearly equal to sixteen English inches or feet.

6.—To reduce French Cube Measure to English.

$$\begin{array}{l} \text{The Paris cube} \\ \text{foot} \dots\dots \end{array} \left. \vphantom{\begin{array}{l} \text{The Paris cube} \\ \text{foot} \dots\dots \end{array}} \right\} = 1.211278 \left. \vphantom{1.211278} \right\} \begin{array}{l} \text{English} \\ \text{cubical} \end{array} \left\{ \begin{array}{l} 2093.088384 \\ 1.211378 \end{array} \right\} \text{in.}$$

$$\text{The cubic inch} = .000700 \left. \vphantom{\text{The cubic inch}} \right\} \text{feet, or}$$

7.—To reduce English Cube Measure to French.\*

$$\begin{array}{l} \text{The English cube foot, or} \\ 1728 \text{ cubical inches} \dots \end{array} \left. \vphantom{\begin{array}{l} \text{The English cube foot, or} \\ 1728 \text{ cubical inches} \dots \end{array}} \right\} = 1427.4864 \left. \vphantom{1427.4864} \right\} \begin{array}{l} \text{French cubical} \\ \text{inches.} \end{array}$$

$$\text{The cubical inch} \dots\dots = .8260$$

$$\text{The cube tenth} \dots\dots = .0008$$

§ III.—MEASURE OF CAPACITY.

The Paris pint contains 58.145† English cubical inches, and the English wine pint contains 28.875 cubical inches; or the Paris pint contains 2.0171082 English pints, and the English pint contains .49617 Paris pints; hence,

$$\left. \begin{array}{l} \text{To reduce the Paris pint to the English,} \\ \text{multiply by} \dots\dots\dots \end{array} \right\} 2.0171082$$

$$\left. \begin{array}{l} \text{To reduce the English pint to the Paris,} \\ \text{divide by} \dots\dots\dots \end{array} \right\}$$

The septier of Paris is 7736 French, or 9370.45 English, cubical inches; and the muid is 92832 French, or 112445.4 English cubical inches.

\* To convert the weight of a French cubic foot, of any particular substance, given in French grains, into the corresponding weight of an English cubic foot in English troy grains, multiply the French grains by 0.6773181, and the product is the number of English troy grains contained in an English cubic foot of the same substance.

† It is said by Belidor, *Archit. Hydraul.* to contain 31 oz. 64 grs. of water, which makes it 58.075 English inches; but, as there is considerable uncertainty in the determinations of the weight of the French cubical measure of water, owing to the uncertainty of the standards made use of, it is better to abide by Mr. Everard's measure, which was made by the Exchequer standards, and by the proportions of the English and French foot, as established by the French Academy and Royal Society.

According to Baumé, the Paris pint contains 32 French ounces of water, at the temperature of 54°.5 Fahrenheit; which would make it equal to 59.729 English cubical inches.

*New French Weights and Measures.*1.—*Measures of Length; the Metre being at 32°, and the Foot at 62°.*

	English Inches.
Millimetre =	.03937
Centimetre =	.39371
Decimetre =	3.93708
Metre* =	39.37079
Decametre =	393.70790
Hecatometre =	3937.07900
Kilometre =	39370.79000
Myriometre =	393707.90000

2.—*Measures of Capacity.*

	Cubic Inches.
Millilitre =	.06103
Centilitre =	.61027
Decilitre =	6.10271
Litre† =	61.02705
Decalitre =	610.27052
Hecatolitre =	6102.70515
Kilolitre =	61027.05152
Myriolitre =	610270.51519

3.—*Measures of Weight.*

	English Grains.
Milligramme =	.0154
Centigramme =	.1542
Decigramme =	1.5424
Gramme‡ =	15.4245
Decagramme =	154.2449
Hecatogramme =	1542.4485
Kilogramme =	15424.4852
Myriogramme =	154244.8515

\* Determined by Captain Kater.

† The Litre is the cubic decimetre; and the number here given is the correct cube of 3.937079.

‡ The Gramme is the weight of a millilitre (= .061027) of water at its maximum density. Since a cubic inch of water at 62° weighs 252.458 grains, a millilitre at the same temperature would weigh 15.4067674 grains, which number multiplied by 1.00115 (which expresses the expansion of water from the maximum density to 62°) gives 15.42448515 for the correct weight of the gramme in English grains.

*Specific Gravities of Solid and Liquid Substances.*

For the specific gravities of the acids and other liquid substances, and of the metals, see the respective sections in which they are described. A Table of the sp. gr. of gases is given vol. i. p. 149.

GEMS.		STONES, &c.	
Diamond, white oriental .....	3.5212	Jasper, brown .....	2.6911
Topaz, oriental .....	4.0106	Granite, Egyptian....	2.6541
Sapphire, oriental ..	3.9941	Rock crystal .....	2.6530
Garnet, Bohemian ..	4.1888	Chalcedony, bright ..	2.6640
Beryl, oriental .....	3.5489	Carrara marble .....	2.7168
Hyacinth, common ..	3.6873	Alabaster, oriental....	2.7302
Emerald, from Peru	2.7755	Carnelian .....	2.6137
Crysolithe, from Brasil	2.6923	Slate, common, for roofs	2.8535
Amethyst, oriental ..	2.651	Flint .....	2.5941
Ruby, oriental .....	4.2833	Agate, oriental .....	2.5901
		Portland-stone .....	2.533
		Serpentine, green, Italian .....	2.4295
		Opal, noble .....	2.144
		Pumice-stone .....	0.9145
STONES, &c.			
Ponderous spar .....	4.4300		
Porphyry .....	2.7651		

SALTS.

	Hassenfratz.	Kirwan.	Muschenbroek.	Newton.
Potassa .....	1.7085	4.6215		
Lime .....	1.5233	2.3908	2.3700	
Magnesia .....	0.3460	2.3298		
Alumina .....	0.8200	2.0000		
Baryta .....	2.3740	4.0000		
Sulphate of potassa ..	2.4073	2.636	2.398	
———— alumina	1.7109		1.7260	1.714
———— zinc .....	1.9120		1.9	1.712
———— iron .....	1.8399		1.88	
———— copper ..	2.1943	2.23		
Nitrate of potassa ..	1.9369	1.933	1.901	1.900
Muriate of soda .....	2.2001		2.0835	2.143
Acetate of lead .....	2.3450		2.3953	
Supertart. of potassa	1.9153		1.8745	
Sub-borate of soda ..	1.7230		1.7170	1.714
Carbonate of potassa	2.0120		2.749	
———— soda ..	1.3591	1.421		
———— ammonia	0.9660	1.8245	1.5026	

*Table of Specific Gravities continued.*

GLASSES AND VITRIFICATIONS.	RESINS.
Green bottle-glass .. 2.7325	Guaiacum..... 1.2289
French crystal-glass.. 2.8922	Jalap..... 1.2185
French mirror-glass, from St. Gobin .... 2.4882	Ammoniacum ..... 1.2071
English flint glass .. 3.3203	Benzoë ..... 1.0924
China porcelain..... 2.3847	Sandarac ..... 1.0920
	White resin ..... 1.0819
	Colophony ..... 1.0441
	Mastich ..... 1.0742
	Copal, transparent .. 1.0452
	Elastic resin ..... 0.9335
	INSPISSATED JUICES.
	Aloe, <i>succotrina</i> .... 1.3795
	Opium ..... 1.3366
	WOODS.
	Lignum guaiacum .. 1.3330
	Box wood, Dutch.... 1.3280
	French box wood .... 0.912
	Ebony ..... 1.2090
	Heart of old oak .... 1.1700
	Mahogany ..... 1.063
	Olive tree ..... 0.9270
	Mulberry tree, Spanish 0.8970
	Beech tree..... 0.8520
	Yew tree, Spanish .... 0.8070
	Apple tree..... 0.7930
	Plum tree ..... 0.7850
	Maple tree ..... 0.7550
	Cherry tree ..... 0.7150
	Quince tree ..... 0.7050
	Orange tree ..... 0.7050
	Walnut tree ..... 0.6710
	Pear tree ..... 0.6610
	Cypress, Spanish .... 0.6440
	Pine tree ..... 0.5500
	White Spanish poplar tree ..... 0.5294
	Cork ..... 0.2400
INFLAMMABLES.	
Roll-sulphur..... 1.9907	
Phosphorus ..... 1.714	
Pit-coal ..... 1.3292	
Amber ..... 1.0780	
Heaviest charcoal.... 0.441	
Mineral naphtha .... 0.708	
Camphor ..... 0.9887	
Liquid ammonia .... 0.8970	
ANIMAL FATS, &c.	
Spermaceti ..... 0.9433	
Butter ..... 0.9423	
Tallow ..... 0.9419	
Mutton suet ..... 0.9235	
Train oil ..... 0.9235	
Hogs' lard..... 0.9568	
Ivory..... 1.825	
Bees' wax ..... 0.9648	
GUMS.	
Common gum ..... 1.4817	
Gum Arabic ..... 1.4523	
Gum tragacanth .... 1.3161	
GUM RESINS.	
Assafoetida ..... 1.3275	
Scammonium, from Smyrna ..... 1.2743	
Galbanum ..... 1.2120	

*Table for reducing the Degrees of Baumé's Hydrometer to the Common Standard.*

Baumé's Hydrometer for Liquids lighter than Water.

Temperature 55° Fahrenheit, or 10° Reaumur.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10	1.000	18	.942	26	.892	34	.847
11	.990	19	.935	27	.886	35	.842
12	.985	20	.928	28	.880	36	.837
13	.977	21	.922	29	.874	37	.832
14	.970	22	.915	30	.867	38	.827
15	.963	23	.909	31	.861	39	.822
16	.955	24	.903	32	.856	40	.817
17	.949	25	.897	33	.852		

Baumé's Hydrometer for Liquids heavier than Water.

Temperature 55° Fahrenheit, or 10° Reaumur.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0	1.000	21	1.170	42	1.414	63	1.779
3	1.020	24	1.200	45	1.455	66	1.848
6	1.040	27	1.230	48	1.500	69	1.920
9	1.064	30	1.261	51	1.547	72	2.000
12	1.089	33	1.295	54	1.594		
15	1.114	36	1.333	57	1.659		
18	1.140	39	1.373	60	1.717		

ADMEASUREMENT AND EFFECTS OF HEAT.

1.—*Correspondence between different Thermometers.*

Fahrenheit's thermometer is universally used in this kingdom. In this instrument the range between the freezing and boiling points of water is divided into 180°; and, as the greatest possible degree of cold was supposed to be that produced by mixing snow and muriatic of soda, it was made the zero. Hence the freezing point became 32°, and the boiling point 212°.

The Centigrade thermometer places the zero at the freezing point, and divides the range between the freezing and boiling points into 100°. This scale has long been used in Sweden, under the title of Celsius's thermometer, and is generally adopted on the continent.

Reaumur's thermometer, which was formerly used in France, divides the space between the freezing and boiling of water into 80°, and places the zero at the freezing point. It is now little employed.

De Lisle's thermometer is used in Russia. The graduation begins at the boiling point, and increases towards the freezing point. The boiling point is marked 0, and the freezing point 150°.

Wedgwood's pyrometer is only intended to measure very high temperatures. Its zero corresponds with 1077° of Fahr., and each degree of Wedgwood is equal to 130° of Fahr.

Therefore  $180^{\circ} \text{ F.} = 100^{\circ} \text{ C.} = 80^{\circ} \text{ R.} = 150^{\circ} \text{ D.} = \frac{18}{13} \text{ W.}$

*Rule 1.*—To reduce centigrade degrees to those of Fahrenheit, multiply by 9, and divide by 5, and to the quotient add 32, that is,  $\frac{C \times 9}{5} + 32 = \text{F.}$  Another rule is given vol. i. p. 102, note.

*Rule 2.*—To reduce Fahrenheit's degrees to centigrade,  $\frac{\text{F.} - 32 \times 5}{9} = \text{C.}$

*Rule 3.*—To reduce Reaumur's to Fahrenheit's, we have the following formula,  $\frac{\text{R.} \times 9}{4} + 32 = \text{F.}$

*Rule 4.*—To convert Fahrenheit to Reaumur,  $\frac{\text{F.} - 32 \times 4}{9} = \text{R.}$

*Rule 5.*—To reduce De Lisle's degrees under the boiling point, we have  $\text{F.} = 212 - \frac{\text{D.} \times 6}{5}$ . To reduce those above the boiling point,  $\text{F.} = 212 + \frac{\text{D.} \times 6}{5}$ .

*Rule 6.*—And, inversely, to reduce Fahrenheit's degrees to De Lisle's, under the boiling point,  $\frac{1060 - 5 \text{ F.}}{6} = \text{D.}$ ; above the boiling point,  $\frac{\text{F.} \times 5 - 1060}{6} = \text{D.}$

*Rule 7.*—To reduce Wedgwood's degrees to those of Fahrenheit, we have  $\text{W.} \times 130 + 1077 = \text{F.}$

*Rule 8.*—Inversely, to reduce Fahrenheit to Wedgwood  $\frac{\text{F.} - 1077}{130} = \text{W.}$



*Table of the principal Effects of Heat.*1.—*Freezing Points of Liquids.*

Fahren.		Fahren.	
- 55	Strongest nitric acid freezes (Cavendish)	7	Common salt 1, water 4
- 46	Æther and liquid ammonia	8	Sal ammoniac 1, water 4
- 45.5	Nitric acid, sp. gr. 1.424	16	Oil of turpentine (Macquer)
- 45	Sulphuric acid, sp. gr. 1.6415	20	Strong wines
- 39	Mercury	23	Fluoric acid
- 36	Sulphuric acid (Thomson)		Oils bergamot and cinnamon
- 30	Nitric acid, sp. gr. 1.407	25	Human blood
- 22	Acetous acid	28	Vinegar
- 11	2 alcohol, 1 water	30	Milk
- 7	Brandy	32	Water
+ 1	Strongest sulphuric acid (Cavendish)	36	Olive oil
4	Common salt 1 part, water 3 parts	42	Sulphuric acid, sp. gr. 1.741
		46	Ditto ditto, 1.78 (Keir)
		50	Strong acetic acid
		64	Oil of aniseeds, 50 (Thomson)

2.—*Melting Points of Solids.*

Fah.		Fahren.	Wedg.	
40	Equal parts of sulphur and phosphorus	283	..	Tin and bismuth, equal parts
82	Adipocire of muscle	303	..	Camphor
97	Lard (Nicholson)	334	..	Tin 3, lead 2, or tin 2, bismuth 1
90	Phosphorus	442	..	Tin (Chrichton) 413 (Irvine)
104	Resin of bile	460	..	Tin 1, lead 4
109	Myrtle wax (Cadet)	476	..	Bismuth (Irvine)
	Stearin from hog's lard	612	..	Lead (Chrichton) 594 (Irvine) 540 (Newton)
112	Spermaceti (Bostock)		..	Zinc (Davy) 698 (Brogniart)
127	Tallow (Nicholson) 92 (Thomson)	680	..	Antimony
149	Bees' wax	3809	21	Brass
145	Ambergris (La Grange)	4587	27	Copper
150	Potassium	3937	22	Silver
155	Bleached wax (Nicholson)	5237	32	Gold
190	Sodium	17977	130	Cobalt
212	Bismuth 5 parts, tin 3, lead 2	20577	150	Nickel
218	Sulphur (Dr. Thomson)	21097	154	Soft nails
234	Sulphur (Hope) 212 (Fourcroy) 185 (Kirwan)	21637	158	Iron
235	Adipocire of biliary calculi (Fourcroy)	21877	160	Manganese
		23177	+ 170	Platinum, tungsten, molybdena, uranium, titanium, &c.

3.—*Solids and Liquids volatilized.*

Fah.		Fah.	
96	Æther boils	248	Nitric acid boils
126	Bisulphuret of carbon boils	283	White arsenic sublimes
140	Liquid ammonia boils	316	Oil of turpentine boils (Ure)
145	Camphor sublimes (Venturi)	540	Metallic arsenic sublimes
170	Sulphur evaporates (Kirwan)	554	Phosphorus boils
176	Alcohol boils, 174 (Black) 173 (sp. gr. .800)	570	Sulphur boils
212	Water and most essential oils boil	590	Sulphuric acid boils (Dalton) 546 (Black)
219	Phosphorus distils (Pelletier)	600	Linseed oil boils, sulphur sublimes (Davy)
225	Water saturated with common salt boils	660	Mercury boils (Dalton) 644 (Secondat) 600 (Black) 672 (Irvine) 656 (Petit and Dulong)
230	Muriate of lime boils (Dalton)		
242	Nitrous acid boils		

4.—*Boiling Points of saturated Solutions of Salts; by Mr. Griffiths. (Quart. Journ. xviii. 89.)*

Name of Salt.	Dry Salt in 100 parts.	Boiling point.	Name of Salt.	Dry Salt in 100 parts.	Boiling point.
Acid boracic .....	{Not deter- mined}	218°	Nitrate of strontia ....	53	224
Acetate of copper ....	16.5	214	Oxalate of ammonia ..	29	218
— lead .....	41.5	215	— potassa ....	40	220
— soda .....	60	256 } highest	Phosphate of soda ....	{Not deter- mined}	222
Alum .....	52	220	Prussiate of mercury ..	35	214
Borate of soda .....	52.5	222	— (triple) of potassa	55	218
Carbonate of soda ....	{Not deter- mined}	220	Sulphate of copper ....	45	216
Chlorate of potassa ....	40	218	— (proto-) of iron	64	216
Chloride (bi-) of mer- cury .....	{Not deter- mined}	214	— magnesia ..	57.5	222
Chloride of ammonia ....	30	224	— nickel .....	65	235
Muriate of ammonia ..	50	236	— potassa ....	17.5	215
— baryta .....	45	220	— soda .....	31.5	213 } lowest
Nitrate of baryta .....	26.5	214	— zinc .....	45	220
— lead .....	52.5	216	Sulphate (bi-) of potassa	45	220
— potassa ....	74	238	Tartrate of potassa ...	68	234
— soda .....	60	246	— potassa } and soda .....	90	240
			Tartrate (bi-) of potassa	9.5	214

5.—*Miscellaneous Effects of Heat.*

Fahr.		Fahren.	Wedg.	
-90	Greatest cold produced by Mr. Walker	800	..	Hydrogen burns, 1000 (Thomson)
-50	Natural cold observed at Hudson's Bay	802	..	Charcoal burns (Thomson)
-23	Observed on the surface of the snow at Glasgow, 1780	1050		Iron red in twilight, 1035 (Davy)
-14	At Glasgow, 1780	1207	1	Iron red in day light
0	Equal parts snow and salt (or 3, or even 7, below 0°)	1337	+ 2	Azotic gas burns
+ 43	Phosphorus burns slowly	1857	6	Enamel colours burned
59	Vinous fermentation begins	2897	14	Diamond burns (M'Kenzie) 30 W. = 5000 F. (Morveau)
66	to 135, Animal putrefaction	6277	40	Delft ware fired
75	to 80, Summer heat in this climate	8487	57	Working heat of plate glass
77	Vinous fermentation rapid, acetous begins	10177	70	Flint glass furnace
80	Phosphorus burns in oxygen, 104 (Gottling)	12257	86	Cream-coloured ware fired
88	Acetification ceases	13297	94	Worcester china vitrified
96	to 100, Animal temperature	14337	102	Stone ware fired
107	Feverish heat	14727	105	Chelsea china fired
122	Phosphorus burns vividly (Fourcroy) 148 (Thomson)	15637	112	Derby china fired
165	Albumen coagulates, 156 (Black)	15897	114	Flint glass furnace greatest heat
303	Sulphur burns slowly	16007	121	Bow china vitrified
635	Lowest heat of ignition of iron in the dark	16807	124	Plate glass greatest heat
		17327	125	Smith's forge
		20577	150	Hessian crucible fused
		25127	185	Greatest heat observed

*Elasticity of Aqueous Vapour below 32° according to Dalton.*

Tempera- ture.	orce of vap. in inches of mercury.	Tempera- ture.	Force of vap. in inches of mercury.	Tempera- ture.	Force of vap. in inches of mercury.	Tempera- ture.	Force of vap. in inches of mercury.
-40°	0.013	5°	0.076	14°	0.104	23°	0.144
-30	0.020	6	0.079	15	0.108	24	0.150
-20	0.030	7	0.082	16	0.112	25	0.156
-10	0.043	8	0.085	17	0.116	26	0.162
0	0.064	9	0.087	18	0.120	27	0.168
1	0.066	10	0.090	19	0.124	28	0.174
2	0.068	11	0.093	20	0.129	29	0.180
3	0.071	12	0.096	21	0.134	30	0.186
4	0.074	13	0.100	22	0.139	31	0.193

*Table of the Force of Aqueous Vapour above 32° Fahrenheit.*

(From Dr. Thomson's Chemistry, 6th edition, i. 61.)\*

Tempe- rature.	Force of vapour in inches of mercury.				Tempe- rature.	Force of vapour in inches of mercury.			
	Robison.	Dalton.	Ure.	Southern.		Robison.	Dalton.	Ure.	Southern.
32°	0.0	0.200	0.200	0.16	56°		0.458		
33		0.207			57		0.474		
34		0.214			58		0.490		
35		0.221			59		0.507		
36		0.229			60	0.35	0.521	0.516	
37		0.237			61		0.542		
38		0.245			62		0.560		0.52
39		0.254			63		0.578		
40	0.1	0.263	0.250		64		0.597		
41		0.273			65		0.616	0.630	
42		0.283		0.23	66		0.635		
43		0.294			67		0.655		
44		0.305			68		0.676		
45		0.316			69		0.698		
46		0.328			70	0.55	0.721	0.726	
47		0.339			71		0.745		
48		0.351			72		0.770		0.73
49		0.363			73		0.796		
50	0.2	0.375	0.360		74		0.823		
51		0.388			75		0.851	0.860	
52		0.401		0.35	76		0.880		
53		0.415			77		0.910		
54		0.429			78		0.940		
55		0.443	0.416		79		0.971		

\* A Table for practical use is given by Mr. Philip Taylor, *Phil. Mag.* lx. 452.

Table continued.

Temperature.	Force of vapour in inches of mercury.				Temperature.	Force of vapour in inches of mercury.			
	Robison.	Dalton.	Ure.	Southern.		Robison.	Dalton.	Ure.	Southern.
80°	0.82	1.00	1.010		128°		4.11		
81		1.04			129		4.22		
82		1.07		1.02	130	3.95	4.34	4.366	
83		1.10			131		4.47		
84		1.14			132		4.60		4.71
85		1.17	1.170		133		4.73		
86		1.21			134		4.86		
87		1.24			135		5.00	5.070	
88		1.28			136		5.14		
89		1.32			137		5.29		
90	1.18	1.36	1.360		138		5.44		
91		1.40			139		5.59		
92		1.44		1.42	140	5.15	5.74	5.770	
93		1.48			141		5.90		
94		1.53			142		6.05		6.10
95		1.58	1.640		143		6.21		
96		1.63			144		6.37		
97		1.68			145		6.53	6.600	
98		1.74			146		6.70		
99		1.80			147		6.87		
100	1.6	1.86	1.860		148		7.05		
101		1.92			149		7.23		
102		1.98		1.96	150	6.72	7.42	7.530	
103		2.04			151		7.61		
104		2.11			152		7.81		7.90
105		2.18	2.100		153		8.01		
106		2.25			154		8.20		
107		2.32			155		8.40	8.500	
108		2.39			156		8.60		
109		2.46			157		8.81		
110	2.25	2.53	2.456		158		9.02		
111		2.60			159		9.24		
112		2.68		2.66	160	8.65	9.46	9.600	
113		2.76			161		9.68		
114		2.84			162		9.91		10.05
115		2.92	2.810		163		10.15		
116		3.00			164		10.41		
117		3.08			165		10.68	10.800	
118		3.16			166		10.96		
119		3.25			167		11.25		
120	3.0	3.33	3.300		168		11.54		
121		3.42			169		11.83		
122		3.50		3.58	170	11.05	12.13	12.050	
123		3.59			171		12.43		
124		3.69			172		12.73		12.72
125		3.79	3.830		173		13.02		
126		3.89			174		13.32		
127		4.00			175		13.62	13.550	

Table continued.

Temperature.	Force of vapour in inches of mercury.				Temperature.	Force of vapour in inches of mercury.			
	Robison.	Dalton.	Ure.	Southern.		Robison.	Dalton.	Ure.	Southern.
176°		13.92			221.6°			36.700	
177		14.22			222		36.25		
178		14.52			223		36.88		
179		14.83			224		37.53		
180	05	15.15	15.160		225		38.20	39.110	
181		15.50			226		38.89		
182		15.86		16.01	226.3			40.100	
183		16.23			227		39.59		
184		16.61			228		40.30		
185		17.00	16.900		229		41.02		
186		17.40			230	44.5	41.75	43.100	
187		17.80			230.5			43.500	
188		18.20			231		42.49		
189		18.60			232		43.24		
190	17.85	19.00	19.000		233		44.00		
191		19.42			234		44.78		
192		19.86		20.04	234.5			46.800	
193		20.32			235		45.58	47.220	
194		20.77			236		46.39		
195		21.22	21.100		237		47.20		
196		21.68			238		48.02		
197		22.13			238.5			50.30	
198		22.69			239		48.84		
199		23.16			240	54.9	49.67	51.70	
200	22.62	23.64	23.600		242			53.60	
201		24.12			245		53.88	56.34	
202		24.61		24.61	248.5			60.40	
203		25.10			250	66.8	58.21	61.90	60.00
204		25.61			255		62.85	67.25	
205		26.13	25.900		260	80.3	67.73	72.30	
206		26.66			265		72.76	78.04	
207		27.20			270	94.1	77.85	86.30	
208		27.74			275		83.13	93.48	
209		28.29			280	105.9	88.75	101.90	
210	28.65	28.84	28.880		285		94.35		
211		29.41			285.2			112.20	
212		30.00	30.000	30.00	290		100.12	120.15	
213		30.60			293.4				120.00
214		31.21			295		105.97	129.00	
215		31.83			300		111.81	139.70	
216		32.46			305		117.68	150.56	
216.6			33.40		310		123.53	161.30	
217		33.09			312			166.25	
218		33.72			320		135.00		
219		34.35			330				
220	35.8	34.99	35.540		340				
221		35.63			343.6				240.00

*Table of the Elastic Forces of the Vapours of Alcohol, Oil of Turpentine, and Petroleum or Naphtha, in Inches of Mercury. By Dr. Ure. (Phil. Trans. 1818.)*

Alcohol (sp. gr. 0.813.)		Alcohol (specific gravity 0.813.)		Petroleum.	
Temp.	Force of vapours.	Temp.	Force of vapour.	Temp.	Force of vapour.
32°	0.40°	193.3°	46.60°	316°	30.00°
40	0.56	196.3	50.10	320	31.70
45	0.70	200	53.00	325	34.00
50	0.86	206	60.10	330	36.40
55	1.00	210	65.00	335	38.90
60	1.23	214	69.30	340	41.60
65	1.49	216	72.20	345	44.10
70	1.76	220	78.50	350	46.86
75	2.10	225	87.50	355	50.20
80	2.45	230	94.10	360	53.30
85	2.93	232	97.10	365	56.90
90	3.40	236	103.60	370	60.70
95	3.90	238	106.90	372	61.90
100	4.50	240	111.24	375	64.00
105	5.20	244	118.20	Oil of Turpentine.	
110	6.00	247	122.10	Temp.	Force.
115	7.10	248	126.10	304°	30.00°
120	8.10	249.7	131.40	307.6	32.60
125	9.25	250	132.30	310	33.50
130	10.60	252	138.60	315	35.20
135	12.15	254.3	143.70	320	37.06
140	13.90	258.6	151.60	322	37.80
145	15.95	260	155.20	326	40.20
150	18.00	262	161.40	330	42.10
155	20.30	264	166.10	336	45.00
160	22.60			340	47.30
165	25.40			343	49.40
170	28.30			347	51.70
173	30.00			350	53.80
178.3	33.50			354	56.60
180	34.73			357	58.70
182.3	36.40			360	60.80
185.3	39.90			362	62.40
190	43.20				

*New Table, by Mr. Dalton, of the Forces of Vapours in contact with the generating Liquids at different Temperatures.*

Temperatures by the common thermometer.	Ether vapour, ratio 2, specific gravity .72.	Sulphuret of carbon vapour, ratio 1.978.	Alcohol vapour, ratio 2.7, specific gravity .82.	Acetic acid vapour, ratio 2.57.	Water, ratio 2.602.
	Inches of mercury.	Inches of mercury.	Inches of mercury.	Inches of merc.	Inches of merc.
7°	3.75	3.134	.193	..	.11
35	7.5	6.20	.560	.27	.29
65 +	15.	12.26	1.51	.69	.75
97	30.	24.26	4.07	1.77 <sup>1</sup>	1.95
133	60.	48.	11.00	4.54	5 07
173	120.	..	29.70	11.7	13.18
220	240.	..	80.2	30.	34.2
272	..	..	..	..	88.9
340	..	..	..	..	231.0

The above is an improved and extended table of the force of vapour. It shows that the different vapours increase in force in geometrical progression, to certain intervals of temperature, the same to most or all liquids. These intervals of temperature were presumed in a former table to be in reality equal to one another ; but the accuracy of this last notion has been questioned.

*Table, by Mr. Dalton, shewing the Expansion of Air and the Elastic Force of Aqueous and Ethereal Vapour, at different Temperatures.*

Temperature.	Volume of air.	Utmost force of aqueous vapour.	Utmost force of ethereal vapour.	Weight of 100 cubic inches of aqueous vapour.	Temperature.	Volume of air.	Utmost force of aqueous vapour.	Utmost force of ethereal vapour.	Weight of 100 cubic inches of aqueous vapour.
		Inc. merc.	Inc. of merc.	Grains.			Inc. merc.	Inc. of merc.	Grains.
-23°	420				53	501	.54	11.34	.354
-20	428				54	502	.56	11.59	.366
-10	438				55	503	.58	11.85	.378
0	448	.08			56	504	.59	12.12	.384
10	458	.12			57	505	.61	12.39	.396
20	468	.17			58	506	.62	12.66	.402
30	478	.24			59	507	.64	12.94	.414
					60	508	.65	13.22	.420
32°	480	.26	7.00	.178	61	509	.67	13.51	.432
33	481	.27	7.18	.184	62	510	.69	13.80	.444
34	482	.28	7.36	.191	63	511	.71	14.10	.456
35	483	.29	7.54	.197	64	512	.73	14.41	.468
36	484	.30	7.73	.203	65	513	.75	14.72	.480
37	485	.31	7.92	.209	66	514	.77	15.04	.492
38	486	.32	8.11	.216	67	515	.80	15.36	.509
39	487	.33	8.30	.222	68	516	.82	15.68	.521
40	488	.34	8.50	.229	69	517	.85	15.90	.539
41	489	.35	8.70	.235	70	518	.87	16.23	.551
42	490	.37	8.90	.245	71	519	.90	16.56	.569
43	491	.38	9.10	.255	72	520	.92	17.00	.580
44	492	.40	9.31	.267	73	521	.95	17.35	.598
45	493	.41	9.52	.275	74	522	.97	17.71	.610
46	494	.43	9.74	.284	75	523	1.00	18.08	.627
47	495	.44	9.96	.293	76	524	1.03	18.45	.645
48	496	.46	10.18	.303	77	525	1.06	18.83	.662
49	497	.47	10.41	.313	78	526	1.09	19.21	.680
50	498	.49	10.64	.323	79	527	1.12	19.60	.700
51	499	.50	10.87	.329	80	528	1.16	20.00	.721
52	500	.52	11.10	.341					

*“Applications of the preceding Table.*

“These tables will be found of great use in reducing volumes of air from one temperature or pressure to any other given one ; also in determining the specific gravities of dry gases from experiments on those saturated with or containing given quantities of aqueous or other vapours.

“As several writers, and some of considerable eminence, have given erroneous or imperfect formulæ on these subjects, more particularly with regard to the effect of aqueous vapour in modifying the weights and volumes of gases, it has been thought proper to subjoin the following precepts and examples for the use of those who are not sufficiently conversant in such calculations.

“The fifth column of the preceding table, or weight of aqueous vapour, is new, and may therefore require explanation. Gay Lussac is considered the best authority in regard to the specific gravity of steam ; but it would be well if his results were confirmed or corrected, as they are of importance. According to his experience, the specific gravities of common air and of pure aqueous vapour, *of the same temperature and pressure*, are as 8 to 5, or as 1 to .625. Now I assume that 100 cubic inches of common air, free from moisture, of the temperature 60°, and the pressure of 30 inches of mercury, weigh 31 grains nearly. It is an extraordinary fact, that philosophers are not agreed upon the absolute weight of a given volume of common air. Most authors now assume the weight of 100 inches = 30.5 grains, whilst, according to my experience, it is more than 31 grains. If common air be assumed 31 grains, steam would be 19 $\frac{3}{8}$  grains for 100 cubic inches, at the same temperature and pressure, could it subsist ; but, as it cannot sustain that pressure at the temperature of 60°, we must deduct according to the diminished pressure, the utmost force of steam at 60° being .65 parts of an inch of mercury, we have 30 inches : 19 $\frac{3}{8}$  grains :: .65 : .420 grains = the weight of 100 cubic inches of aqueous vapour at 60°, and pressure .65 parts of an inch, which is the number given in the table. The like calculation is required for any other pressure ; but, in addition to this, there is to be an allowance for the temperature from the second column :—Thus, let the weight of 100 cubic inches of steam at 32° be required. We have 30 inches : 19 $\frac{3}{8}$  grains :: .26 inches : .1679 grains ; the weight of 100 inches of steam at 60° ; then if 480 : 508 :: .1679 : .178 grains = weight of 100 cubic inches of steam at 32°, and pressure .26 parts of an inch, the tabular number required.

*“ Examples.*

“1. How many cubic inches of air at 60° are equivalent in weight to 100 cubic inches at 45°?

“By the column headed *volume of air*, we have this proportion, if 493 : 508 :: 100 inches : 103.04 inches, the volume required.

“2. How many cubic inches of air, with the barometer at 30 inches height, are equal in weight to 100 cubic inches when the barometer stands at 28.9 inches ?



“Rule.—The volume of air being inversely as the pressure, we have 30 : 28.9 :: 100 inches : 96½ inches the answer.

“3. How many cubic inches of dry air are there in 100 inches of vapourized air (air saturated with aqueous vapour), at the temperature of 50°, and pressure 30 inches of mercury ?

“Here the formula  $\frac{p-f}{p}$  applies, where  $p$  denotes the atmospheric pressure at the time, and  $f$  denotes the utmost force of vapour in contact with water at the temperature. Hence  $p = 30$ ,  $f = .49$  per table, and we have  $\frac{p-f}{p} = \frac{30 - .49}{30} = \frac{29.51}{30} = 98\frac{1}{3}\frac{1}{10}$ , or

98½ per cent. dry air.

And  $1\frac{2}{3}\frac{1}{10}$  vapour.

100.

If the vapour of ether is assumed, then  $f = 10.64$ , and we have  $\frac{p-f}{p} = \frac{30 - 10.64}{30} = \frac{19.36}{30} = .645$ , or 64½ per cent. dry air.\*

35½ per cent. ethereal vapour.

100

“4. Suppose we find by trial the weight of 100 cubic inches of common air saturated with vapour at 60°, the barometer standing at 30 inches to be 30.5 grains, and the weight of hydrogen gas in like circumstances to be 2.118 grains ; query the weights of 100 cubic inches of each gas free from vapour, and their specific gravities, the temperature and pressure being as above ?

“If 30.5 : 2.118 :: 1 : .0694 = specific gravity of vapourized hydrogen, that of vapourized air being 1. Subtracting .42 grains (weight of vapour per table) from 30.5 grains, leaves 30.08 grains ; and subtracting .65 parts of an inch from 30 inches, leaves 29.35 inches. Hence 100 cubic inches of dry air, at the pressure of 29.35 inches, weigh 30.08 grains ; and we have 29.35 : 30 :: 30.08 : 30.746 grains, the weight of 100 inches of dry air. Again, subtracting .42 grains from 2.118, leaves 1.698 grains = weight of 100 cubic inches of hydrogen of 60°, and sustaining the pressure of 29.35 inches ; whence if 29.35 : 30 :: 1.698 : 1.736 grains, weight of 100 inches of dry hydrogen ; and 30.746 : 1.736 :: 1 : .05645 = specific gravity of dry hydrogen, that of dry air being unity. Or the results may be exhibited as under :

Weight of 100 cubic inches.	Specific Gravities.
Vapourized air ..... 30.5 grains	1 .. 14.4
Vapourized hydrogen 2.118 grains	.0694 .. 1.
Dry air..... 30.746 grains	1 .. 17.7
Dry hydrogen ..... 1.736 grains	.05645.. 1.”

(Dalton's New System, vol. ii. published in 1827.)

\* The aqueous vapour in this case may be considered as insignificant.

*Table of the Expansion of Liquids from 32° to 212°, their bulk at 32° being supposed 1.*

Liquids.	Authority.	Dilatation in decimals.	Dilat. in vulg. frac.
Muriatic acid (sp. gr. 1.137)	Dalton .....	0.06000	$\frac{1}{17}$
Nitric acid (sp. gr. 1.40)	Ditto .....	0.11000	$\frac{1}{9}$
Sulphuric acid (sp. gr. 1.85)	Ditto .....	0.06000	$\frac{1}{17}$
Alcohol .....	Ditto .....	0.11000	$\frac{1}{9}$
Water .....	Ditto .....	0.04600	$\frac{1}{22}$
Water saturated with com- mon salt .....	} Ditto .....	0.05000	$\frac{1}{20}$
Sulphuric ether .....	Ditto .....	0.07000	$\frac{1}{14}$
Fixed oils .....	Ditto .....	0.08000	$\frac{1}{12}$
Oil of turpentine .....	Ditto .....	0.07000	$\frac{1}{14}$
Mercury .....	Ditto .....	0.02000	$\frac{1}{50}$
Ditto .....	Ld. C. Cavendish	0.01872	$\frac{1}{53}$
Ditto .....	Shuckburgh, &c.	0.01852	$\frac{1}{54}$
Ditto .....	Gen. Roy .....	0.01680	$\frac{1}{59}$
Ditto .....	Haellstroem .....	0.01758	$\frac{1}{56}$
Ditto .....	Lalande .....	0.01500	$\frac{1}{66}$
Ditto .....	Petit and Dulong	0.0180180	$\frac{1}{55.50}$

*Dr. Young's Table of the Expansion of Water from the Experiments of Gilpin and Kirwan.*

N. B. Denoting a degree of Fahrenheit's Thermometer, by *f*, the expansion of water, reckoning either way from + 39° is nearly represented by .0000022 *f*<sup>2</sup> - .00000000435 *f*<sup>3</sup>.

Temp.	Observed expansion.	Calculated.
30 G. ....	.00020 .....	.00018
32 G. ....	.00012 .....	.00011
34 G. ....	.00006 .....	.00005
39 G. ....	.00000 .....	.00000
44 G. ....	.00006 .....	.00005
48 G. ....	.00018 .....	.00018
49 G. ....	.00022 .....	.00022
54 G. ....	.00049 .....	.00048
59 G. ....	.00086 .....	.00084
64 G. ....	.00133 .....	.00130
69 G. ....	.00188 .....	.00186
74 G. ....	.00251 .....	.00251
79 G. ....	.00321 .....	.00326
90 G. ....	.00491 .....	.00513
100 G. ....	.00692 .....	.00720
102 G. ....	.00760 .....	.00763
122 G. ....	.01258 .....	.01264
142 G. ....	.01833 .....	.01859
162 G. ....	.02481 .....	.02512
182 G. ....	.03198 .....	.03219
202 G. ....	.04005 .....	.03961
212 G. ....	.04333 .....	.04322

*Table by De Luc, exhibiting the Degrees marked upon Thermometers filled with different Liquids at the same Temperature.*

N. B. To comprehend the meaning of this table, it must be understood that different thermometers (each filled with the particular fluid marked at the tops of the columns, and each being divided into 80 equal parts between the freezing and boiling water points), are placed with their bulbs in the same vessel full of water, and that the water is gradually heated. Then when the mercurial thermometer is at  $5^{\circ}$ ,  $10^{\circ}$ ,  $15^{\circ}$ , &c. the surfaces of the fluids in the other thermometers will be found at the degrees which stand on the same levels. For instance, when the mercurial thermometer stands at  $40^{\circ}$  the water thermometer will be found at  $20.5^{\circ}$ ; the spirit thermometer at  $35.1^{\circ}$ ; the oil thermometer at  $39.2^{\circ}$ , &c.

Mercury.	Olive oil.	Essential oil of chamomile.	Essential oil of thyme.	Alcohol capable of firing gunpowder.	Water saturated with common salt.	Water.
80. <sup>o</sup>	80. <sup>o</sup>	80. <sup>o</sup>	80. <sup>o</sup>	80. <sup>o</sup>	80. <sup>o</sup>	80. <sup>o</sup>
75	74.6	74.7	74.3	73.8	74.1	71.0
70	69.4	69.5	68.8	67.8	68.4	62.0
65	64.4	64.3	63.5	61.9	62.6	53.5
60	59.3	59.1	58.3	56.2	57.1	45.8
55	54.2	53.9	53.3	50.7	51.7	38.5
50	49.2	48.8	48.3	45.3	46.6	32.0
45	44.0	43.6	43.4	40.2	41.2	26.1
40	39.2	38.6	38.4	35.1	36.3	20.5
35	34.2	33.6	33.5	30.3	31.3	15.9
30	29.3	28.7	28.6	25.6	26.5	11.2
25	24.3	23.8	23.8	21.0	21.9	7.3
20	19.3	18.9	19.0	16.5	17.3	4.1
15	14.4	14.1	14.2	12.2	12.8	1.6
10	9.5	9.3	9.4	7.9	8.4	0.2
5	4.7	4.6	4.7	3.9	4.2	0.4
0	0.0	0.0	0.0	0.0	0.0	0.0
- 5				- 3.9	- 4.1	
-10				- 7.7	- 8.0	

*Table of the Expansion of Solids by Heat.*

N. B. The linear expansion by being heated from 32° to 212° Faht. is here to be understood. The expansion in volume may be learned by multiplying the decimal quantities by 3, or dividing the denominators of the vulgar fractions by 3.

Substances tried.	Authority.	Dilatation in Decimals + the original length.	Dil. in vulgar fract.
Antimony .....	Smeaton .....	1.00108300	$\frac{1}{915}$
Bismuth .....	Ditto .....	1.00189200	$\frac{1}{718}$
Brass .....	Lavoisier and Laplace ..	1.00186671	$\frac{1}{535}$
— cast .....	Smeaton .....	1.00187500	$\frac{1}{533}$
— wire .....	Ditto .....	1.00193000	$\frac{1}{518}$
— 16, tin 1 .....	Ditto .....	1.00190800	$\frac{1}{523}$
Copper .....	Lavoisier .....	1.00172244	$\frac{1}{581}$
— hammered .....	Smeaton .....	1.00170000	$\frac{1}{582}$
— .....	Petit and Dulong .....	1.00171821	$\frac{1}{582}$
Glass tube without } lead (crown) .....	Lavoisier .....	1.00087572	$\frac{1}{1144}$
— white barom. ....	Smeaton .....	1.00083000	$\frac{1}{1203}$
— .....	General Roy .....	1.00077615	$\frac{1}{1288}$
— rod .....	Ditto .....	1.00080787	$\frac{1}{1237}$
— English flint .....	Lavoisier .....	1.00081166	$\frac{1}{1248}$
— crown .....	Ditto .....	1.00089760	$\frac{1}{1144}$
— tube .....	Petit and Dulong .....	1.00086130	$\frac{1}{1166}$
Gold, Paris standard } not softened .....	Lavoisier .....	1.00155155	$\frac{1}{645}$
— pure .....	Ditto .....	1.00146606	$\frac{1}{682}$
Iron .....	Smeaton .....	1.00125800	$\frac{1}{796}$
Ditto .....	Petit and Dulong .....	1.00118203	$\frac{1}{846}$
— cast (prism) .....	General Roy .....	1.00110940	$\frac{1}{901}$
— hammered .....	Lavoisier .....	1.00122045	$\frac{1}{819}$
— wire .....	Ditto .....	1.00123504	$\frac{1}{812}$
Lead .....	Ditto .....	1.00284836	$\frac{1}{351}$
Ditto .....	Smeaton .....	1.00286700	$\frac{1}{348}$
Pewter, fine .....	Ditto .....	1.002283	$\frac{1}{438}$
Palladium .....	Wollaston .....	1.0010000	$\frac{1}{1000}$
Platinum .....	Troughton .....	1.00099180	$\frac{1}{1008}$
Ditto .....	Borda .....	1.00085655	$\frac{1}{1167}$
Ditto .....	Petit and Dulong .....	1.0088420	$\frac{1}{1131}$
Silver, Paris standard..	Lavoisier .....	1.00190868	$\frac{1}{523}$
Ditto .....	Troughton .....	1.0020826	$\frac{1}{480}$
Solder, soft, (lead 2, tin 1)	Smeaton .....	1.0025080	$\frac{1}{398}$
— spelter, (brass 2, zinc 1)	Ditto .....	1.0020580	$\frac{1}{486}$
Speculum metal .....	Ditto .....	1.00193300	$\frac{1}{517}$
Steel, hard .....	Lavoisier .....	1.00107875	$\frac{1}{917}$
— ditto .....	Smeaton .....	1.00122500	$\frac{1}{816}$
— soft .....	Lavoisier .....	1.00107956	$\frac{1}{928}$
— tempered .....	Ditto .....	1.00123956	$\frac{1}{807}$
Tin, Falmouth .....	Lavoisier .....	1.00217298	$\frac{1}{462}$
— Malacca .....	Ditto .....	1.00193765	$\frac{1}{516}$
— Grain .....	Smeaton .....	1.00248300	$\frac{1}{402}$
Zinc .....	Ditto .....	1.00294200	$\frac{1}{338}$
— hammered half } inch per foot .....	Ditto .....	1.00301100	$\frac{1}{337}$

*Tables exhibiting a collective View of all the Frigorific Mixtures contained in Mr. Walker's Publication, 1808.*

Communicated by Mr. Walker.

1.—*Table, consisting of Frigorific Mixtures, having the Power of generating, or creating Cold, without the Aid of Ice, sufficient for all useful and Philosophical Purposes, in any part of the World at any Season.*

Frigorific Mixtures without Ice.

MIXTURES.	Thermometer sinks.	Degree of cold produced.
Muriate of ammonia 5 parts Nitrate of potassa .. 5 Water ..... 16	From + 50° to + 10°	40
Muriate of ammonia 5 parts Nitrate of potassa .. 5 Sulphate of soda.... 8 Water ..... 16	From + 50° to + 4°	46
Nitrate of ammonia 1 part Water ..... 1	From + 50° to + 4°	46
Nitrate of ammonia 1 part Carbonate of soda .. 1 Water ..... 1	From + 50° to - 7°	57
Sulphate of soda.... 3 parts Diluted nitric acid.. 2	From + 50° to - 3°	53
Sulphate of soda.... 6 parts Muriate of ammonia 4 Nitrate of potassa .. 2 Diluted nitric acid.. 4	From + 50° to 10°	60
Sulphate of soda.... 6 parts Nitrate of ammonia 5 Diluted nitric acid.. 4	From + 50° to - 11°	64
Phosphate of soda .. 9 parts Diluted nitric acid.. 4	From + 50° to - 12°	62
Phosphate of soda .. 9 parts Nitrate of ammonia 6 Diluted nitric acid.. 4	From + 50° to - 21°	71
Sulphate of soda .. 8 parts Muriatic acid ..... 5	From + 50° to 0°	50
Sulphate of soda.... 5 parts Diluted sulphuric acid 4	From 50° to + 3°	47

N. B.—If the materials are mixed at a warmer temperature than that expressed in the Table, the effect will be proportionally greater; thus, if the most powerful of these mixtures be made when the air is + 85°, it will sink the thermometer to + 2°. The ingredients best adapted for freezing creams, cooling wines, &c. because recoverable for any number of times with unimpaired powers, consist of equal parts nitrate of potassa (saltpetre) and muriate of ammonia (sal ammoniac). Some useful directions for applying freezing mixtures to these purposes are given by Mr. Walker, in the Phil. Mag. and Ann. Phil. June, 1828.

2.—Table consisting of *Frigorific Mixtures, composed of Ice, with chemical Salts and Acids.*

Frigorific Mixtures with Ice.

MIXTURES.	Thermometer sinks.	Degrees of cold produced.
Snow, or pounded ice, 2 parts Muriate of soda . . . . . 1	From any Temperature.	to $-5^{\circ}$ *
Snow, or pounded ice, 5 parts Muriate of soda . . . . . 2 Muriate of ammonia 1		to $-12^{\circ}$ *
Snow, or pounded ice, 24 parts Muriate of soda . . . . . 10 Muriate of ammonia 5 Nitrate of potassa .. 5		to $-18^{\circ}$ *
Snow, or pounded ice, 12 parts Muriate of soda . . . . . 5 Nitrate of ammonia .. 5		to $-25^{\circ}$ *
Snow . . . . . 3 parts Diluted sulphuric acid 2	From $+32^{\circ}$ to $-23^{\circ}$	55
Snow . . . . . 8 parts Muriatic acid . . . . . 5	From $+32^{\circ}$ to $-27^{\circ}$	59
Snow . . . . . 7 parts Diluted nitric acid .. 4	From $+32^{\circ}$ to $-30^{\circ}$	62
Snow . . . . . 4 parts Muriate of lime . . . . . 5	From $+32^{\circ}$ to $-40^{\circ}$	72
Snow . . . . . 2 parts Cryst. muriate of lime 3	From $+32^{\circ}$ to $-50^{\circ}$	82
Snow . . . . . 3 parts Potassa . . . . . 4	From $+32^{\circ}$ to $-51^{\circ}$	83

N.B.—The reason for the omissions in the last column of this table, is the thermometer sinking in these mixtures to the degree mentioned in the preceding column, and never lower, whatever may be the temperature of the materials at mixing.

3.—*Table consisting of Frigorific Mixtures selected from the foregoing Tables, and combined, so as to increase or extend Cold to the extremest Degrees.*

Combinations of Frigorific Mixtures.

MIXTURES.	Thermometer sinks.	Degrees of cold produced.
Phosphate of soda.... 5 parts Nitrate of ammonia .. 3 Diluted nitric acid .. 4	From 0° to - 34°	34
Phosphate of soda.... 3 parts Nitrate of ammonia .. 2 Diluted mixed acids.. 4	From - 34° to - 50°	16
Snow..... 3 parts Diluted nitric acid .. 2	From 0° to - 46°	46
Snow..... 8 parts Diluted sulphuric acid 3 Diluted nitric acid .. 3	From - 10° to - 56°	46
Snow..... 1 part Diluted sulphuric acid 1	From - 20° to - 60°	40
Snow..... 3 parts Muriate of lime ..... 4	From + 20° to - 48°	68
Snow..... 3 parts Muriate of lime ..... 4	From + 10° to - 54°	64
Snow..... 2 parts Muriate of lime ..... 3	From - 15° to - 68°	53
Snow..... 1 part Cryst. muriate of lime 2	From 0° to - 66°	66
Snow..... 1 part Cryst. muriate of lime 3	From - 40° to - 73°	33
Snow..... 8 parts Diluted sulphuric acid 10	From - 68° to - 91°	23

N.B.—The materials in the first column are to be cooled, previously to mixing, to the temperature required, by mixtures taken from either of the preceding tables.

Table of the Solubility of some Salts, &amp;c

NAMES OF SALTS.	Solubility in 100 parts water.		NAMES OF SALTS.	Solub. of Ice,	
	At 60°	At 512°		At 60°	
<b>ACIDS.</b>			<b>SALTS.</b>		
Arsenic .....	150.		Chloride of sodium..	35.42	40.
Benzoic .....	0.208	4 17	strontia.....	150.	Unlimit.
Boracic .....		2.	Muriate of ammonia	33.	100.
Camphoric .....	1.04	3.3	Nitrate of ammonia	59.	200.
Citric .....	133.	200.	baryta .....	8.	25.
Gallic.....	8.3	66.	lime .....	400.	
Mucic .....	0.84	1.25	magnesia ...	100.	+ 100.
Molybdenic .....		0.1	potassa .....	14.25	100.
Oxalic .....	6.		soda .....	33.	+ 100.
Suberic .....	0.69	50.	strontia.....	100.	200.
Succinic.....	4.	50.	Oxalate of strontia..	0.1 $\frac{1}{4}$	
Tartaric .....	Very sol.		Phosphate of am-}		
			monia .....	25.	+ 25.
			baryta .....	0.	0.
<b>SALIFIABLE BASES.</b>			lime .....	0.	0.
Baryta .....	5.	50.	Phosphate of mag-}		
crystallized ..	57.	Unlimit.	nesia .....	66.	
Lime .....	0.2		potassa .....	Very sol.	
Potassa .....	Very sol.		soda .....	25.	50.
Soda .....	do.		strontia.....	0.	0.
Strontia.....	0.6		Phosphite of ammonia	50.	+ 50.
crystallized ..	1.9	50.	baryta .....	0.4	
			potassa .....	33.	+ 33.
<b>SALTS.</b>			Sulphate of ammonia	50.	+ 100.
Acetate of ammonia	Very sol.		baryta .....	0.002	
baryta .....	do.		copper .....	25.	50.
lime .....	do.		iron .....	50.	+ 100.
magnesia ..	do.		lead .....	0.1 $\frac{1}{4}$	
potassa .....	100.		lime .....	0.2	0.22
Acetate of soda .....	Very sol.		magnesia ...	100.	644.
strontia.....		40.	potassa .....	10.	26.
Carbon. of ammonia	+ 30.	100.	soda .....	37.	125.
baryta .....	Insoluble		strontia.....	0.	0.02
lime .....	do.		Sulphite of ammonia	100.	
magnesia ...	0.04	0.01111	lime .....	0.125	
potassa .....	25.		magnesia ...	5.	
soda .....	50.	+ 100.	potassa .....	100.	
strontia .....	Insoluble		soda .....	25.	100.
Camphorate of am-}			Saccholactate of po-}		
monia .....	1.	33.	tassa .....		12.
baryta .....	0.16		soda .....		20.
lime .....	0.5		Sub-borate of soda }		
potassa .....	33.	+ 33.	(berax) .....	8.4	16.8
Citrate of soda.....	60.		Super-sulphate of }		
lime .....	Insoluble		alumina and po-}		
Chlorate of baryta ..	25.	+ 25.	tassa (alum).... }	5.	133.
mercury .....	25.		potassa .....	50.	+ 100.
potassa .....	6.	40.	Super-oxalate of }		
soda .....	35.	+ 35.	potassa .....		10.
Chloride of barium..	34.	59.	tartrate of }		
lead .....	4.5		potassa .....	1.3	3.3
lime .....	200.		Tartrate of potassa..	25.	
magnesium ..	100.		and soda ...	20.	
mercury .....	5.	50.	antimony & }		
potassium....	34.	59.	potassa .....	6.6	33.
silver .....	0.3 $\frac{1}{4}$				

\* This Table, from the impossibility of finding sufficient data, I am aware is very incomplete; and, in several instances, I have little doubt that the degrees of solubility assigned are erroneous. The subject requires investigation, and, if properly pursued, would no doubt furnish many important results. A very successful beginning has been made by Gay Lussac, see Ann. of Phil. vol. xv.



3.—*Table of Substances soluble in Alcohol.*

fo

(See also p. 378, 379.)

NAMES OF SUBSTANCES.	Temperature.	100 parts alcohol dissolve
Acetate of copper.....	176°	7.5
soda.....	176	46.
Arsenate of potassa.....	do.	3.75
soda.....	do.	1.7
Boracic acid.....	do.	20.
Camphor.....	do.	75.
Muriate of ammonia.....	do.	7.
alumina.....	54½	100.
copper.....	176	100.
iron.....	176	100.
lime.....	do.	100.
magnesia.....	do.	547.
mercury.....		88.3
zinc.....	54½	100.
Nitrate of ammonia.....	176	89.2
alumina.....	54½	100.
cobalt.....	54½	100.
lime.....		125.
potassa.....	176	2.9
silver.....	do.	41.7
Succinic acid.....	do.	74.
Sugar, refined.....	do.	24½
Super-oxalate of potassa.....		3.
Tartrate of potassa.....		0.04

OTHER SUBSTANCES SOLUBLE IN ALCOHOL.—All the acids, except the sulphuric and nitric, which decompose it, and the phosphoric and metallic acids.—Potassa, soda, and ammonia, very soluble. Soaps; extract; tan; volatile oils; adipocire; resins; urea.

SUBSTANCES INSOLUBLE, OR VERY SPARINGLY SOLUBLE, IN ALCOHOL.—Earths; phosphoric and metallic acids; almost all sulphates and carbonates; the nitrates of lead and mercury; the chlorides of lead, silver, and sodium (the last, *per* Chenevix, sparingly soluble); the subborate of soda; the tartrate of soda and potassa, and super-tartrate of potassa; fixed oils; wax; starch; gum; caoutchouc; woody fibre; gelatine; albumen, and gluten.

sol. in Water.\*

*Table of Incompatible Salts.*

SALTS.	INCOMPATIBLE WITH	Solubility in 100 parts water. At 212°
1. Fixed alkaline sulphates . . . . .	{ Nitrates of lime and magnes. Muriates of lime and magnesia.	1.
2. Sulphate of lime . . . . .	{ Alkalis, Carbonate of magnesia, Muriate of baryta.	
3. Alum . . . . .	{ Alkalis, Muriate, &c. of baryta, Nitrate, muriate, carbonate of lime, Carbonate of magnesia.	
4. Sulphate of magnesia . . . . .	{ Alkalis, Muriate, &c. of baryta, Nitrate and muriate of lime.	
5. Sulphate of iron . . . . .	{ Alkalis, Muriate, &c. of baryta, Earthy carbonates.	
6. Muriate of baryta . . . . .	{ Sulphates, Alkaline carbonates, Earthy carbonates.	
7. Muriate of lime . . . . .	{ Sulphates, except of lime, Alkaline carbonates, Carbonate of magnesia.	
8. Muriate of magnesia . . . . .	{ Alkaline carbonates, Alkaline sulphates.	
9. Nitrate of lime . . . . .	{ Alkaline carbonates, Carbonates of magnesia & alumina, Sulphates, except of lime.	

*Table of Equivalents.*

In the following *Table of Chemical Equivalents*, which, under another view, may be considered as denoting the *relative weights of the atoms of bodies*, hydrogen is expressed by 1, and other bodies are referred to it as a standard. This appears to me more convenient than the employment of oxygen as the unit of comparison, because all bodies lighter than oxygen are, in the latter case, necessarily expressed by fractional numbers. It is easy, however, to reduce the one scale to the other by the rule of proportion. Thus, to convert the numbers on the

\* That is, salts which cannot exist together in solution, without mutual decomposition. This incompatibility, however, it is to be understood, exists only in solutions of a certain density.

their equivalents on the oxygen scale, multiply and divide the product by 8: for example, 23 (the representing iron, hydrogen = 1)  $\times 10 = 230 \div 8 =$  the scale, which takes oxygen as 10. To convert the oxygen to the hydrogen numbers, reverse the operation, multiplying by 8, and dividing by 10.

In drawing up the table, I have had recourse to the best authorities, both original and compiled. The most copious tables hitherto published are those of Dr. Thomson,\* Mr. Phillips,† M. Berzelius,‡ and Mr. Brande.§ In many instances, their numbers, as well as my own, are to be considered merely as approximations, especially in the case of organic bodies; and there are, probably, few numbers which will not undergo alteration, as the instruments and operations of chemistry become more refined and correct. In practice, the table will be rendered much more useful, if accompanied by a *logometric sliding scale*, the application of which to this purpose was a happy invention of Dr. Wollaston. On the fixed part of this instrument may be inscribed, opposite to their equivalent numbers, the names of substances; but, as it is not possible to include on a single scale the names of all substances, those may be selected which are most important, and most likely to become subjects of reference. Or, by a little practice, a scale containing *numbers only* may be used with facility, the names of substances being in this case *imagined* to be placed on the fixed part of the instrument, opposite to their representative figures; and it has this great advantage, that it does not require alteration to accommodate it to improved numbers. A scale, however, on which names are inscribed, is best adapted to beginners; and an instrument of this kind will be found capable of affording a great variety of information, important both to scientific and practical chemists, to the latter of whom very minute alterations in equivalent numbers are not of importance.

1. The quantity of any substance, which is equivalent to a given quantity of any other inscribed on the scale, may be learned by inspection; the quantities taken being quite arbitrary, and such as suit the purpose of the moment. For example, by bringing 50 on the slider opposite to magnesia, or

\* First Princ. of Chem. vol. ii.

‡ Ann. de Ch. &c. Aug. 1828.

† Ann. of Phil. N.S. vol. x. p. 293.

§ In 1 vol. 8vo. 1828.

to its equivalent 20, it will be seen that 50 parts of that earth are equivalent to 70 lime, 120 potassa, &c.

2. It shows the quantity of each base that is equivalent to a given quantity of any acid. Thus 50 on the slider being brought opposite to sulphuric acid, or to its equivalent 40, it appears that 50 parts of that acid saturate 25 of magnesia, 35 lime, 60 potassa, &c. In a similar manner, the scale indicates the quantities of different acids required to saturate each base; thus 50 parts of magnesia saturate 100 of sulphuric acid, 135 nitric, &c.

3. It enables us to determine by inspection the proportions of the components in a given quantity of any substance of known composition. Thus, by bringing 100 on the slider opposite to 72, the equivalent of dry sulphate of soda, we find 55.5 on the slider opposite to the equivalent of sulphuric acid, and 44.5 opposite to the equivalent of soda, numbers which together make up 100 of the salt.

4. It expresses not only the *proximate*, but the *ultimate*, elements of compounds. Thus, keeping the slider in the same situation as in the last case, we find 22.4 on the slider opposite to 16, the equivalent of sulphur, and 33.1 opposite to 24, the equivalent of three proportions of oxygen; and  $22.4 + 33.1$  make up together 55.5 sulphuric acid. By reference to the equivalents of sodium and oxygen, we find also that 44 parts of soda are made up of 33 sodium and 11 oxygen.

5. The quantity of any substance, which we must take to decompose a given quantity of another by single elective attraction, is at once taught by the scale. Thus, if we wish to know the smallest quantity of sulphuric acid adequate to decompose 100 parts of chloride of sodium, by bringing 100 on the slider opposite to chloride of sodium, or its equivalent 60, we find  $66\frac{1}{2}$  on the slider opposite to 40, the equivalent of dry sulphuric acid; and opposite to 49, the equivalent of sulphuric acid of commerce, we find  $81\frac{1}{2}$  on the slider. We must, therefore, employ  $66\frac{1}{2}$  of the former, or  $81\frac{1}{2}$  of the latter. Again, to know the quantity of dry sulphate of soda, which would result if all the common salt were decomposed, we shall find 120 on the slider opposite to the dry sulphate, or to its equivalent 72, and 270 opposite to the crystallized sulphate, or to its representative number 162. In several cases, however, in order to effect a complete decomposition, it is necessary to employ more

than the equivalent quantity of the decomposing body. (See vol. i. p. 61, 348.)

6. The quantities of salts, each consisting of two ingredients, that are required for mutual decomposition, may be learned by a similar use of the sliding scale. Supposing, for instance, that we have 83 parts of sulphate of potassa, and wish to know the quantity of chloride of barium required for their decomposition; bring 83 on the slider opposite to sulphate of potassa, or to 88, its representative, and opposite to 106, the equivalent of chloride of barium, we find 100 on the slider, which is the number required. The results of this decomposition may also be learned by examining the instrument when in the same situation of the slider; for opposite to the equivalent of sulphate of baryta 118, we find on the slider 111, and opposite to chloride of potassium we find 71.5 on the slider, the two last numbers indicating the resulting quantities of the new compounds. Again, from the weight of a precipitate, it is easy to deduce the quantities of salts which have afforded it. Thus, if we had obtained by experiment 120 parts of dry sulphate of baryta, on bringing that number opposite to its equivalent 118, we see at once that they may have resulted from  $89\frac{1}{2}$  of sulphate of potassa, and 108 of chloride of barium; and, moreover, that 120 parts of barytic sulphate are composed of 40.6 sulphuric acid, and 79.4 baryta; the sulphuric acid consisting of 16.5 sulphur and 24.1 oxygen, and the baryta of 8.15 oxygen and 71.25 barium.

Other applications of the scale of equivalents are pointed out by Dr. Wollaston, in a memoir, explaining its principle and uses, inserted in the Philosophical Transactions for 1814.

*Table of Chemical Equivalents or Atomic Weights.*

(Hydrogen = 1.)

Acid, acetic real (51 Prout).....	50	Acid, chloro-cyanic.....	62
crystallized, 1 water ....	59	chromic, 1 chr. + 3 ox. ....	52
arsenic .....	62	citric, dry .....	58
arsenious .....	54	crystals, 2 water .....	76
benzoic .....	120	columbic?.....	152
boracic, 2 ox.? .....	24	cyanic, 1 cy. + 1 ox. ....	34
crystals 2, water ..	42	ferro-cyanic?.....	108
bromic, 1 b. + 5 ox.....	115	fluoric? .....	10
carbonic, 1 c. + 2 ox.....	22	fluoboric? .....	34
chloric, 1 chl. + 5 ox.....	76	fluosilicic .....	26
chloriodic? 1 chl. + 1 iod.	161	formic.....	37
chloro-carbonic, 1 c. ox. +		fulminic. See cyanic.	
1 chl. ....	50	gallic? .....	63

Acid, hydriodic .....	126	Ammonia, carbonate, 1 am. + 1 c. a.	39
hydrobromic .....	76	chlorate, dry .....	93
hydrochloric .....	37	chloro-carbonate .....	67
hydro-cyanic, 1 cy. + 1 hyd.	27	citrate, dry .....	75
hydro-fluoric .....	19	fluoborate, do. ....	51
hydro-phosphorous, 2 ph.		hydriodate .....	143
acid 1 water .....	49	iodate .....	182
hyponitrous, 1 nit. + 3 ox.	38	muriate, 1 am. + 1 m. a.	54
hypophosphorous, 2p. + 1 ox.	32	nitrate, dry.....	71
hyposulphurous, 1 s. + 1 ox.	24	crystallized, 1 water..	80
hyposulphuric, 2 s. + 5 ox.	72	oxalate, dry.....	53
iodic, 1 iod. + 5 ox. ....	165	crystals, 2 water ....	71
malic .....	59	phosphate, dry .....	45
manganeseous .....	52	crystals, 2 water ....	63
manganestic .....	60	phosphite, dry .....	37
molybdic .....	72	sesqui-carbonate .....	100
molybdous .....	64	crystals, 2 water ....	118
muriatic .....	37	succinate, dry.....	67
nitric, real, 1 n. + 5 ox. ..	54	crystals, 2 water ...	85
(sp. gr. 1.5.) 2 water ..	72	sulphate, dry .....	57
nitrous, 1 n. + 4 ox. ....	46	crystals, 2 water.....	75
oxalic, dry.....	36	sulphite, dry .....	49
crystals (3 w. Berz. and		tartrate, do. ....	83
Prout) .....	63	Antimony (J. Davy).....	44
perchloric, 1 chl. + 7 ox. ..	92	chloride .....	80
phosphoric, 1 p. + 2 ox. ...	28	deutoxide, 1 anty. + 1½	
phosphorous, 1 p. + 1 ox. ..	20	ox. ....	56
prussic. See hydrocyanic.		hydrosulphuret .....	69
purpuric.....	44	iodide .....	168
pyro-uric?.....	251	peroxide, 1 ant. + 2 ox.	60
saccholactic .....	105	protoxide, 1 ant. + 1 ox.	52
selenic, 1 s. + 3 ox. ....	64	sulphuret, 1 ant. + 1 s.	60
selenious, 1 s. + 2 ox. ....	56	tartarized, T. 2 water..	354
succinic .....	50	Phill. 3 water,	363
sulphocyanic? .....	59	Arseniate of potassa, dry .....	110
sulpho-naphthalic .....	208	soda, do. ....	94
sulphovinic .....	108	Arsenic.....	38
sulphuric, dry, 1 s. + 3 ox.	40	chloride of?.....	74
(sp. gr. 1.849) 1 water ..	49	iodide?.....	162
sulphurous, 1 s. + 2 ox. ..	32	sulphuret (orpiment).....	54
sulphocyanic.....	57	sesqui-sulph. (realgar) ...	62
tantallic. See columbic.		Azote.....	14
tartaric, dry ..	66	Barium .....	70
crystals, 1 water .....	75	(Berz. and Turner) ....	68.86
titanic? .....	48	chloride of, 1 b. + 1 chl..	106
tungstic .....	120	iodide (Turner) .....	195
uric? .....	72	peroxide, 1 b. + 2 ox. ....	86
Alcohol, 4 ol. gas + 2 aq. vapour	46	phosphuret .....	82
Alum, dry .....	262	protoxide, 1 b. + 1 ox....	78
crystallized, 25 water ..	487	sulphuret .....	86
ammoniacal .....	231	Baryta, dry, 1 barium + 1 ox. ..	78
cryst., 24 water .....	447	(Berz.) .....	76.86
soda .....	228	crystallized, 20 water ..	258
cryst., 28 water .....	580	acetate, dry (Turner) ....	128
Alumina (27 Phillips) .....	18	cryst., 3 water.....	155
sulphate .....	58	arseniate? dry .....	140
Aluminum (18 Phillips) .....	10	arsenite? do. ....	132
Ammonia .....	17	binhyposulphite, 1 b. + 2 ac.	126
acetate .....	67	biphosphate, dry.....	134
bicarbonate, 1 am. + 2		carbonate, do.....	100
c. a. ....	61	chlorate, do. ....	154
cryst. 2 water.....	79	chromate, do. ....	130
binoxalate, 8 water ....	161	hydrate, cryst., 20 water..	258
biphosphate, dry .....	73	hydriodate, dry .....	203

Baryta, iodate, dry.....	242	Chlorine .....	36
nitrate cryst., no water ..	132	hydrate, 10 water .....	126
oxalate, dry.....	114	protoxide, 1 c. + 1 ox. . .	44
cryst. 3 water .....	141	peroxide, 1 c. + 4 ox. ? . .	68
ferro-cyanate ? .....	145	Chromium (Thomson) .....	28
muriate, cryst., 1 water. . .	124	protoxide. . . . .	36
phosphate, dry .....	106	deutoxide (T.) .....	44
phosphite, do. ....	98	sulphuret.....	44
crystallized, 1 water. . . .	107	Cobalt (Rothoff).....	30
seleniate .....	134	arseniate, dry.....	100
succinate .....	128	chloride .....	66
sulphate, dry .....	118	nitrate, dry .....	92
(Berz.).....	116.86	oxalate, do. ....	74
sulphite, dry .....	110	peroxide, 1 c. + 1½ ox. . .	42
tartrate, do. ....	144	phosphate, dry .....	66
tungstate, do. ....	198	protoxide, 1 c. + 1 ox. . . .	38
Bismuth (John Davy) .....	72	sulphate, dry .....	78
chloride, 1 b. + 1 chl. . . .	108	crystallized, 7 water. . . .	147
iodate .....	245	sulphuret.....	46
iodide .....	197	Chloride of nitrogen, 4 chl. + 1 n.	158
nitrate, dry .....	134	Columbium ? .....	144
cryst. 3 water.....	161	Copper (32 Thomson) .....	64
oxalate, do. ....	116	acetate, 1 ac. + 1 perox. . .	130
oxide.....	80	cryst., 6 water.....	184
phosphate.....	108	binacetate, 2 ac. + 1 perox.	180
cryst., 3 water .....	135	cryst., 3 water .....	207
subsulphate, 3 ox. b. +		biphosphate, 2 water.....	126
1 ac.....	280	bisulphate (blue vitriol) ..	160
sulphate, dry .....	120	cryst., 10 water.....	250
sulphuret.....	88	bisulphuret, 1 c. + 2 s. . .	96
Borax (biboate of soda) .....	88	binitrate, 1 perox. + 2 ac.	188
cryst., 8 water .....	152	iodide .....	188
Boron ? .....	8	perchloride, 1 c. + 2 chl. . .	136
Bromine (See p. 688).....	75	protochloride, 1 c. + 1 chl. .	100
Cadmium (Stromeyer) .....	56	protoxide, 1 c. + 1 ox. . . .	72
chloride .....	92	peroxide, 1 c. + 2 ox. . . .	80
nitrate, dry.....	118	subnitrate, dry, 4 perox. +	
oxide .....	64	1 ac.....	374
phosphate, dry .....	92	subacetate, 2 perox. + 1 ac.	210
sulphate, do. ....	104	subsulphate, 2 perox. + 1 ac.	200
sulphuret, 1 c. + 1 s. . . .	72	sulphate. See bisulphate.	
Calcium .....	20	Corrosive sublimate. See Mercury.	
chloride .....	56	Cyanogen, 1 nitr. + 2 carb. . . .	26
fluoride (fluor spar) . . .	38	Ether, sulphuric, 4 ol. gas + 1 aq.	
iodide .....	145	vap. ....	37
oxide (lime).....	28	muriatic, 1 ol. gas + 1 m. a.	44
phosphuret .....	32	chloric, 1 ol. gas + 1 chl. . .	43
sulphuret .....	36	Fluoride of boron .....	24
Calomel, see Mercury, protochloride.		of calcium .....	38
Carbon .....	6	Fluorine ? .....	18
bisulphuret, 1 car. + 2 s. . .	38	Glucina .....	26
hydriodide .....	139	Glucinum .....	18
hydrochloride .....	43	Gold ? .....	200
oxide (gas) 1 c. + 1 ox. . .	14	chloride .....	236
perchloride, 2 car. + 3 chl. .	120	iodide .....	325
protochloride, 1 + 1 chl. . .	42	protoxide, 1 gold + 1 ox. . .	208
subchloride, 2 + 1 chl. . . .	48	peroxide, 1 + 3 .....	224
Carbureted hydrogen, light, 1 car.		perchloride .....	272
+ 2 hyd. ....	8	sulphuret, 1 gold + 3 sul. . .	248
Carbureted hydrogen, olefant, 2		Gum (Ure 68).....	90
car. + 2 hydr. ....	14	Hydrogen .....	1
Cerium (Thomson) .....	50	Iodine .....	125
protoxide.....	58	Iridium (T.) .....	30
peroxide ? .....	62	oxide .....	38

Iron .....	28	Lime, tungstate .....	178
protochloride, 1 ir. + 1 chl.	64	Lithia .....	18
perchloride, 1 ir. + 1½ .....	82	carbonate .....	40
protoxide, 1 ir. + 1 ox. ....	36	nitrate, dry .....	72
peroxide, 1 ir. + 1½ .....	40	phosphate .....	46
persulphate, 1 perox. + 1½ ac.	100	sulphate, dry.....	58
protosulphuret, 1 ir. + 1 s. ....	44	cryst., 1 water.....	67
persulphuret, 1 ir. + 2 s. ....	60	Lithium.....	10
subsulphate, 4 perox. + 1 ac.	204	chloride .....	46
sulphate, dry, 1 prot. + 1 ac.	76	sulphuret .....	26
cryst., 7 water.....	139	Magnesia, 1 magnesium + 1 ox.	20
Lead .....	104	ammonia phosphate ...	93
acetate, dry.....	162	cryst., 5 water .....	138
cryst., 3 water .....	189	dried in air, 4 water..	129
arseniate, dry .....	174	ammonia-sulph.....	116
carbonate, do. ....	134	cryst., 7 water . ....	179
chloride.....	140	carbonate, dry, 1 + 1 ac.	42
chromate, dry, 1 prot. + 1 ac.	164	cryst., 3 water .....	69
bichromate, do. 1 + 2 ac. ..	216	common. See vol. i. p. 640,	182
subchromate, 2 prot. + 1 ac.	276	chloride, dry .....	56
deutoxide, 1 lead + 1½ ox. .	116	hydrate, 1 m. + 1 water	29
gallate .....	175	muriate .....	57
hyponitrite .....	150	nitrate, dry.....	74
cryst., 1 water .....	159	phosphate, do.....	48
malate, dry .....	172	sulphate, do. ....	60
molybdate, do. ....	184	cryst., 7 water .....	123
nitrate, cryst., no water ...	166	tartrate .....	87
nitrite .....	450	Magnesium .....	12
oxalate, dry.....	148	chloride .....	48
peroxide, 1 lead + 2 ox. ....	120	iodide .....	137
phosphate, dry.....	140	Manganese .....	28
phosphite .....	132	carbonate, 1 protox. +	
protoxide, 1 lead + 1 ox. ..	112	1 ac.....	58
subnitrate .....	278	chloride, 1 m. + 1 chl.	64
sub-trit-acetate, 3 protox. +		deutoxide (brown) 1 m.	
1 ac. ....	386	+ 1½ .....	40
sulphate, dry .....	152	iodide .....	153
sulphite, do. ....	144	oxalate, dry.....	72
sulphuret .....	120	phosphate, do. ....	64
tartrate, dry.....	178	protoxide, green, 1 m.	
Lime, 1 calcium + 1 ox. ....	28	+ 1 ox. ....	36
acetate, dry .....	78	peroxide, 1 m. + 2 ox.	44
arseniate.....	90	sulphate, 1 protox. +	
binhyposulphite, 6 water ..	130	1 ac.....	76
biphosphate, dry .....	84	cryst., 5 water .....	121
carbonate, do. ....	50	sulphuret .....	44
chlorate, do. ....	104	sulphd. protoxide ...	80
chloride, 1 + 1.....	64	Mercury .....	200
citrate, dry.....	86	bichloride (corrosive subl.)	272
chromate, do. ....	80	bicyanide, 1 m. + 2 cy. ..	252
hydrate, 1 + 1.....	37	binitrate, 1 prot. + 2 ac.	324
hydrog. sulphuret .....	89	bi-persulphate, dry.....	296
iodate .....	193	bisulphuret (cinnabar) ..	232
muriate .....	65	iodide .....	325
cryst., 5 water .....	110	perbisulphate .....	296
oxalate, dry .....	64	periodide .....	450
phosphate, do. ....	56	perchloride (corr. sub.) ..	272
phosphite, do. ....	48	peroxide, 1 m. + 2 ox. ..	216
subchloride, 2 l. + 1 chl. ..	92	persulphate .....	256
6 water .....	146	protochloride (calomel) ..	236
sulphate, dry.....	68	protonitrate, 1 prot. +	
cryst., 2 water .....	86	1 ac. ....	262
tartrate .....	94	cryst., 2 water .....	280
4 water .....	130	perbinitrate .....	324



Mercury, protosulphate, 1 prot. + 1 ac. ....	248	Potassa, biphosphate, dry.....	104
protosulphate .....	248	bisulphate, do. ....	128
cryst., 2 water .....	266	cryst., 2 water .....	146
protoxide, 1 m. + 1 ox. ....	208	bitartrate.....	180
subprotosulphate.....	470	cryst., 1 water .....	189
sulphate .....	256	carbonate, 1 + 1 ac. ..	70
sulphuret .....	216	cryst., 2 water .....	88
Molybdenum .....	48	chlorate, dry .....	124
protoxide.....	56	chromate, do.....	100
Morphia .....	322	citrate, do. ....	106
Nickel (Rothoff).....	30	hydrate, solid, 1 water..	57
acetate, dry.....	102	hydriodate, dry .....	174
arsenate, do. ....	114	iodate, do. ....	213
carbonate, do.....	66	molybdate, do. ....	120
chloride, do.....	80	muriate .....	85
nitrate, do.....	98	nitrate cryst., no water	102
cryst. ....	143	oxalate, do. 1 + 1 ac. ..	84
oxalate, dry.....	80	perchlorate, do.....	140
peroxide (38 T.).....	56	phosphate, do.....	76
protoxide (34 T.) .....	52	quadroxalate, do. 1 + 4 ac.	192
sulphate, dry .....	92	subcarbonate. See Carbonate.	
cryst., 7 water .....	155	succinate, do. ....	98
sulphuret .....	60	sulphate, do. ....	88
Nitric oxide, 1 n. + 2 o. ....	30	sulphite, do. ....	80
Nitrogen .....	14	tartrate, do. ....	114
protoxide .....	22	tungstate, do.....	198
deutoxide.....	30	Potassium.....	40
Nitrous gas. See Nitric oxide.		chloride .....	76
oxide, 1 n. + 1 o.....	22	cyanide.....	74
Oil, olive ? .....	79	iodide .....	165
Olefiant gas (2 hyd. + 2 c.) .....	14	peroxide, 1 p. + 3 ox. ..	64
Osmium ? .....		phosphuret, 1 + 1 .....	52
oxide.....		protoxide, dry, 1 + 1..	48
Oxygen.....	8	subphosphuret, 2 + 1..	92
Palladium ? .....	56	sulphurets, various.	
oxide ? .....	64	Rhodium ? .....	44
Phosphorus .....	12	protoxide ? .....	52
carburet .....	18	peroxide ? .....	60
chloride .....	48	Selenium .....	40
perchloride .....	84	Selenureted hydrogen .....	41
sulphuret ....	28	Silica.....	16
bi-hydruret, 1 p. + 2 hyd. (See p. 692) .....	14	Silicium or silicon .....	8
hydruret, 1 p. + 1 h. ....	13	Silver .....	110
Platinum .....	96	chlorate, dry .....	194
ammonia muriate .....	222	chloride, do. ....	146
bisulphuret .....	128	iodate, do. ....	283
perchloride .....	168	iodide, do. ....	235
peroxide .....	112	nitrate, do. ....	172
protochloride .....	132	oxalate, do .....	154
protoxide.....	104	protoxide, 1 + 1.....	118
sulphuret.....	112	suboxide, 3 s. + 2 ox.....	346
persulphuret .....	128	phosphate, dry .....	146
Potassa, dry, 1 potassium + 1 ox. ....	48	sulphate, do. ....	158
arsenate, dry (164)....	110	sulphuret .....	126
arsenite, do. (148).....	102	Soda, 1 sodium + 1 ox. ....	32
benzoate cryst., 13 water, 195		acetate, dry .....	82
bicarbonate, do. 1 + 2 ac. ....	92	cryst., 6 water .....	136
cryst., 1 water.....	101	arsenate, dry .....	94
binarsenate, dry .....	172	arsenite, do. ....	86
cryst., 1 water .....	181	cryst., 8 water .....	166
bichromate, dry .....	152	biborate .....	80
binoxalate, do. 1 + 2 ac. ....	120	cryst., 8 water .....	152
		bicarbonate, dry .....	76
		cryst., 2 water .....	94

Soda, binarseniate .....	156	Sulphureted hydrogen .....	17
cryst., 5 water .....	201	carbon. See Carbon.	
carbonate (sub-carb.) dry ..	54	Tannin ? .....	71
cryst., 10 water .....	144	Tellurium .....	32
sesquicarbonate, 2 water ..	83	chloride .....	68
chlorate, dry .....	103	oxide ..	40
chromate .....	84	Tin .....	58
cryst., 12 water .....	192	bisulphuret .....	90
hydrate .....	41	peroxide, 1 tin + 2 ox. ....	74
hydriodate, dry .....	158	protoxide, 1 tin + 1 ox. ....	66
iodate, do. ....	197	perchloride, 1 tin + 2 chl. ..	130
nitrate, do. ....	86	protochloride, 1 + 1 .....	94
oxalate, do. ....	68	sulphuret .....	74
sulphate, do. ....	72	Titanium (Thomson) .....	32
cryst., 10 water .....	162	bisulphuret .....	64
sulphite, dry .....	64	protoxide .....	40
tartrate, do. ....	98	titanic acid .....	48
tartarized. 114 + 98 .....	212	Tungsten .....	126
Sodium .....	24	bisulphuret .....	158
chloride .....	60	oxide, 1 t. + 2 ox. ....	142
iodide .....	148	Uranium .....	208
peroxide, 1 s. + 1½ ox. ....	36	oxide ? .....	216
protoxide, 1 s. + 1 ox. ....	32	Water .....	9
Starch ? .....		Yttria .....	42
Strontia .....	52	Yttrium .....	34
carbonate, dry .....	74	Zinc .....	34
hydrate, 1 water .....	61	carbonate .....	64
muriate .....	89	chloride .....	70
cryst., 8 water .....	161	hydriodate, dry .....	168
nitrate, dry .....	106	iodide .....	158
oxalate, do. ....	88	iodate, dry .....	198
phosphate, do. ....	80	nitrate, do. ....	96
sulphate, do. ....	92	oxalate, do. ....	78
Strontium .....	44	oxide .....	42
chloride .....	80	phosphate, dry .....	70
oxide .....	52	phosphuret .....	46
Strychnia ? .....	380	sulphate, dry .....	82
Sugar (Prout 75) .....	81	cryst., 7 water .....	145
Sulphur .....	16	sulphite, dry .....	74
chloride, 1 sulph. + 1 chl. ....	52	sulphuret .....	50
iodide .....	140	Zirconia .....	48
phosphuret .....	28	Zirconium .....	40

*Berzelius's Table of the Atomic Weights of Simple Bodies,  
and of their Combinations with Oxygen.*

(Ann. de Chim. et de Phys. Août, 1828.)

The following Table has been compiled by Berzelius from the most recent, and what he deems the most correct, experimental results. As the standard, which its author has adopted for oxygen, and his peculiar views of the atomic constitution of bodies, appear to be gaining ground over most parts of the continent of Europe, I have deemed it necessary to give the Table, with no other alteration than that of an alphabetical arrangement. Mere inspection of the numbers comprised in it is not enough for a comparison of them, with the numbers

given in the foregoing Table; partly because Berzelius, by taking for granted that equal volumes of oxygen and hydrogen contain the same number of atoms, necessarily doubles the relative weight of most bodies to hydrogen as 1; and still more, because many of his equivalent numbers are deduced from different experimental data. The specific gravities of hydrogen and oxygen gases, for instance, he determines to be as 1 to 16.026, thus introducing fractions into the whole scale of equivalent numbers, which refers to hydrogen as unity.

Again, the theoretical views, taken by Berzelius of many compounds, differ from those adopted in this country. Alumina, for instance, which is generally regarded by British chemists as composed of an atom of metallic base + an atom of oxygen, Berzelius considers as a compound of 2 atoms of base + 3 atoms of oxygen, or as a sesqui-oxide. It is necessary, therefore, before attempting to compare his numbers with those in the foregoing scale, to ascertain in every case what atomic constitution he assigns to the body in question; and this may be learned from the symbol which stands opposite to it. Subtracting, then, the weight of the atom or atoms of oxygen, we have the weight of the atom or atoms of base. Thus, if from 642.334 (the equivalent of alumina) we take 300, we have 342.344 for the weight of two atoms of alumina, and 171.167 for that of a single atom. In all the instances marked † in the following Table, the numbers in the fourth column are reducible to the scale most common in this country, on which 2 volumes of hydrogen are equivalent to an atom, by merely halving them. The letter S implies that no reduction is required. To reduce Berzelius's oxygen numbers to the hydrogen scale of this country, multiply by 16.026 and divide the product by 100. To reduce the hydrogen numbers to his scale, divide by 16.026 and multiply the quotient by 100. Thus iodine (oxygen = 100) =  $789.145 \times 16.026 = 12646.8377$ , which, divided by 100, =  $126.468377$ , the equivalent of iodine on the hydrogen scale.

The experiments which have led Berzelius to adopt, for the relative weights of hydrogen and oxygen gases, the numbers 1 and 16.026, may possibly be nearer the truth than those agreeing with the proportions of 1 to 16. But it is to be regretted that a difference of results, so small as to be greatly within the limits of experimental error, should have been allowed to countervail a general law of so much simplicity, and supported by

so many probabilities, as that *all the elementary numbers, hydrogen being unity, are multiples of the atomic weight of hydrogen by a whole number.*

*Explanation of the Symbols.*—To express the composition of a compound body, Berzelius has proposed signs, which are employed in the annexed Table, and are so much used by chemical writers on the continent, that the knowledge of them is essential, as a key to some of their most interesting memoirs. Each elementary substance is represented by the initial of its Latin name; but when two such substances have the same initial letter, they are distinguished as follows: Combustible bodies, not metallic, are denoted by the first letter alone; such metals, as have the same initial, being designated by a second letter. Thus, C denotes carbon; Co, cobalt; Cu, cuprum, copper; Fe, ferrum, iron; Sn, stannum, tin; Sb, stibium, antimony. O signifies oxygen; but as it is a more general ingredient of compound bodies than any other, Berzelius proposes to mark the number of its atoms by dots placed above the initial letter. Thus,  $\overset{\cdot}{C}$ , or  $C + 1 O$ , = carbonic oxide;  $\overset{\cdot\cdot}{C}$ , or  $C + 2 O$ , = carbonic acid;  $\overset{\cdot\cdot}{Sn}$ , or  $Sn + 2 O$ , = deutoxide of tin. This expedient renders the formulæ shorter and more intelligible. When a compound body contains several molecules of a combustible element, the number of its atoms is annexed on the right, like an exponent in algebra. Thus,  $\overset{\cdot\cdot}{Al} \overset{\cdot\cdot\cdot}{S}^3$  = sulphate of alumina, means that there are three atoms of sulphur, or sulphuric acid, for one of alumina. But if it were required to denote that a body contains, for example, two atoms of the sulphate of alumina, the number is placed on the left; and it then multiplies all the letters which follow it. Thus,  $\overset{\cdot\cdot}{K} \overset{\cdot\cdot\cdot}{S}^2 + 2 \overset{\cdot\cdot}{Al} \overset{\cdot\cdot\cdot}{S}^3$  is the formula exhibiting the composition of alum. A line drawn under the first letter of the symbol of any substance in the table, expresses two atoms; thus,  $\overset{\cdot\cdot}{Mn}$  = two atoms of manganese + 3 atoms of oxygen. The term oxidule is applied to a supposed compound of two atoms of metallic base + one atom of oxygen; and *oxide* to the combination of one atom of each of those elements. Further exemplifications of the use of these symbols may be found in Berzelius's work on Chemical Proportions, and in the article "Proportions Determinate," contributed by him to Dr. Brewster's Encyclopædia.

*Berzelius's Table of Equivalents.*

NAMES.	Symbols.	Oxygen = 100.	1 vol. Hy- drog. 1
Acid arsenious . . . . .	$\ddot{\text{As}}$	1440.084	230.790
antimonious . . . . .	$\ddot{\text{Sb}}$	1006.452	161.296
antimonic . . . . .	$\ddot{\text{Sb}}$	2112.904	338.617
boracic . . . . .	$\ddot{\text{B}}$	871.966	139.743
carbonic . . . . .	$\ddot{\text{C}}$	276.437	44.302 †
chloric . . . . .	$\ddot{\text{Cl}}$	942.650	151.071 †
perchloric . . . . .	$\ddot{\text{Cl}}$	1042.650	167.097
chromic . . . . .	$\ddot{\text{Cr}}$	651.819	104.462 †
columbic . . . . .	$\ddot{\text{Ta}}$	2607.430	417.871
hydro-cyanic . . . . .	$\overline{\text{H}} \text{ N } \underline{\text{C}}$	342.390	54.872 †
hyponitrous . . . . .	$\ddot{\text{N}}$	477.036	76.449 †
hyposulphuric . . . . .	$\ddot{\text{S}}$	902.330	144.609 †
hyposulphurous . . . . .	$\dot{\text{S}}$	301.165	48.265 †
iodic . . . . .	$\ddot{\text{I}}$	2037.562	326.543 †
manganesic . . . . .	$\ddot{\text{Mn}}$	1211.575	194.169
molybdic . . . . .	$\ddot{\text{Mo}}$	898.525	143.999 †
muriatic . . . . .	$\overline{\text{H}} \text{ Cl}$	455.129	72.940 †
nitric . . . . .	$\ddot{\text{N}}$	677.036	108.503 †
oxalic . . . . .	$\ddot{\text{C}}$	452.875	72.578 †
phosphoric . . . . .	$\ddot{\text{P}}$	501.165	80.317
selenic . . . . .	$\ddot{\text{Se}}$	794.582	127.341 †
selenious . . . . .	$\ddot{\text{Se}}$	694.582	111.315 †
sulphuric . . . . .	$\ddot{\text{S}}$	501.165	80.317 †
sulphurous . . . . .	$\dot{\text{S}}$	401.165	64.291 †
titanic . . . . .	$\ddot{\text{Ti}}$	589.092	94.409 †

NAMES.	Symbols.	Oxygen = 100.	1 vol. Hy- drog. = 1.
Alumina .....	$\ddot{\text{Al}}$	642.334	102.942
Aluminum .....	Al	171.167	27.431
Ammonia .....	$\text{N H}^3$	214.474	34.372 †
Antimony .....	Sb	806.452	129.243
oxide .....	$\ddot{\text{Sb}}$	1912.904	306.565
Arsenic .....	As	470.042	75.329 †
Azote (nitrogen) .....	N	88.518	14.186 S
Barium .....	Ba	856.880	137.325 †
Baryta .....	$\dot{\text{Ba}}$	956.880	153.351 †
Bismuth .....	Bi	1330.376	213.208
oxide .....	$\ddot{\text{Bi}}$	2960.752	474.495
Boron .....	B	135.983	21.793
Bromine (See p. 687.) .....	Br	489.150	78.391 S
Cadmium .....	Cd	696.767	111.665 †
oxide .....	$\dot{\text{Cd}}$	796.767	127.691 †
Calcium .....	Ca	256.019	41.030 †
Carbon .....	C	76.437	12.250 †
Cerium .....	Ce	574.718	92.105 †
protoxide .....	$\dot{\text{Ce}}$	674.718	108.132
deutoxide .....	$\ddot{\text{Ce}}$	1449.436	232.289
Chlorine .....	Cl	221.325	35.470 S
Chromium .....	Cr	351.819	56.383 †
oxidule .....	$\ddot{\text{Cr}}$	1003.638	160.845
Cobalt .....	Co	368.991	59.135 †
oxide .....	$\dot{\text{Co}}$	468.991	75.161 †
peroxide .....	$\ddot{\text{Co}}$	1037.982	166.349
Columbium .....	Ta	1153.715	184.896
Copper .....	Cu	395.695	63.415 †

NAMES.	Symbols.	Oxygen = 100.	1 vol. Hy- drog. 1.
Copper, oxidule .....	$\dot{\text{Cu}}$	891.390	142.856 †
oxide .....	$\ddot{\text{Cu}}$	495.695	79.441
Cyanogen .....	$\text{N C}$	329.911	52.872 †
Fluorine .....	$\text{F}$	116.900	18.734 S
Glucina .....	$\ddot{\text{Be}}$	962.958	154.325
Glucinum .....	$\text{Be}$	331.479	53.123 †
Gold .....	$\text{Au}$	1243.013	199.207
oxidule .....	$\dot{\text{Au}}$	2586.026	414.441
oxide .....	$\ddot{\text{Au}}$	2786.026	446.493
Hydrogen .....	$\text{H}$	6.2398	1.000 S
Iodine (See p. 687) .....	$\text{I}$	789.145	126.468 S
Iron .....	$\text{Fe}$	339.213	54.363 †
oxidule .....	$\dot{\text{Fe}}$	439.213	70.389 †
oxide .....	$\ddot{\text{Fe}}$	978.426	156.804
chloride .....	$\text{Fe Cl}$	781.863	125.303 †
perchloride .....	$\text{Fe Cl}^3$	2006.376	321.545
Iron, sulphate of oxidule .....	$\dot{\text{Fe}} \text{ S}$	940.378	150.706
sulphate of oxide .....	$\ddot{\text{Fe}} \text{ S}^3$	2481.906	397.754
Lead .....	$\text{Pb}$	1294.498	207.458 †
oxide .....	$\dot{\text{Pb}}$	1394.498	223.484 †
brown oxide .....	$\ddot{\text{Pb}}$	1494.498	239.511 †
Lime .....	$\dot{\text{Ca}}$	356.019	57.056 †
Lithia .....	$\dot{\text{L}}$	227.757	36.501 †
Lithium .....	$\text{L}$	127.757	20.474 †
Magnesia .....	$\dot{\text{Mg}}$	258.353	41.404 †
Magnesium .....	$\text{Mg}$	158.353	25.378 †
Manganese .....	$\text{Mn}$	355.787	57.019 †
oxidule .....	$\dot{\text{Mn}}$	455.787	73.045 †
oxide .....	$\ddot{\text{M}}$	1011.575	162.117

NAMES.	Symbols.	Oxygen = 100.	1 vol. Hy- drog. = 1.
Manganese, peroxide .....	$\ddot{\text{Mn}}$	555.787	89.071 †
Manganic acid .....	$\text{Mn}$	1211.575	194.169
Mercury .....	Hg	1265.822	202.863 S
chlorure (calomel) .....	$\text{Hg Cl}$	2974.295	475.666 †
chloride (corr. sub.) .....	$\text{Hg Cl}$	1708.472	273.803 S
oxidule .....	$\dot{\text{Hg}}$	2631.645	421.752
oxide .....	$\ddot{\text{Hg}}$	1365.822	218.889 S
Molybdenum .....	Mo	598.525	95.920 †
Nickel .....	Ni	369.675	59.245 †
oxide .....	$\dot{\text{Ni}}$	469.675	75.271 †
Nitrogen .....	N	88.518	14.186 S
oxidule (nitrous oxide) .....	$\dot{\text{N}}$	277.036	44.398 †
oxide (nitrous gas) .....	$\ddot{\text{N}}$	188.518	30.212 S
Oxygen .....	O	100.000	16.026 †
Palladium .....	Pd	714.618	114.526 †
oxide .....	$\dot{\text{Pd}}$	814.618	130.552 †
Phosphorus .....	P	196.155	31.436
Platinum .....	Pt	1215.220	194.753 †
oxide .....	$\ddot{\text{Pt}}$	1415.220	226.806 †
Potassa .....	K	589.916	94.541 †
sulphate .....	$\text{K S}$	1091.081	174.859 †
Potassium .....	K	489.916	78.515 †
peroxide .....	$\ddot{\text{K}}$	789.916	126.593 †
ferro-cyanide .....	$\left. \begin{array}{l} \text{FeNC} + \\ 2 \text{KNC} \end{array} \right\}$	2308.778	370.008
Rhodium .....	R	750.680	120.305
oxide .....	$\ddot{\text{R}}$	1801.360	228.689
Selenium .....	Se	494.582	79.263 †
Silica .....	$\ddot{\text{Si}}$	577.478	92.548
Silicium .....	Si	277.478	44.469



NAMES.	Symbols.	Oxygen = 100.	1 vol. Hy- drog. = 1.
Silver .....	Ag	1351.607	216.611 †
oxide .....	Ag	1451.607	232.637 †
chloride .....	Ag Cl	1572.932	252.081
Soda .....	Na	390.897	62.646 †
Sodium .....	Na	290.897	46.620 †
peroxide .....	Na	881.794	141.318
chloride .....	Na Cl	512.222	
Strontia .....	Sr	647.285	103.735 †
Strontium .....	Sr	547.285	87.709 †
Sulphur .....	S	201.165	32.239 †
Sulphureted hydrogen .....	H S	213.644	34.239 †
Tellurium .....	Te	806.452	129.243
oxide .....	Te	1006.452	161.296
Tin .....	Sn	735.294	117.839
oxidule .....	Sn	835.294	133.866 †
oxide .....	Sn	935.294	149.892 †
Titanium .....	Ti	389.092	62.356 †
Tungsten .....	W	1183.200	189.621
Uranium .....	U	2711.360	434.527
oxidule .....	U	2811.360	450.553
oxide .....	U	5722.720	917.132
Water .....	H	112.479	18.026 †
Yttria .....	Y	501.840	80.425 †
Yttrium .....	Y	401.840	64.395 †
Zinc .....	Zn	403.226	64.621 †
oxide .....	Zn	503.226	80.649 †
Zirconia .....	Zr	1140.476	182.775
Zirconium .....	Zr	420.238	67.348

*Table, showing the Proportions in Volumes of several Compounds whose Elements are gaseous.*

(N. B.—A Table of the Specific Gravities of Gases may be found, Vol. I. p. 149.)

Name.	Proportions in Volumes.	Resulting Volumes.
Air, atmospheric	4 Nitrogen + 1 oxygen	5
Alcohol, vapour	1 Olefiant gas + 1 aq. vapour	1
Ammonia	3 Hydrogen + 1 nitrogen	2
Aqueous vapour (steam)	2 Hydrogen + 1 oxygen	2
Carbonic oxide gas	1 Vapour of carbon + $\frac{1}{2}$ oxygen	1
Do. acid do.	1 Ditto + 1 do.	1
Do. do.	1 Carbonic oxide + $\frac{1}{2}$ oxygen	1
Carbureted hydrogen gas	2 Hydrogen + 1 carbon	1
Carbonate sub- of ammonia	1 Carbonic acid + 2 ammonia	(solid)
Do. of do.	1 Ditto + 1 do.	ditto
Do. sesqui- of do.	1 Ditto + $1\frac{1}{2}$ do.	ditto
Chlorine, protoxide of, gas	1 Oxygen + 2 chlorine	$2\frac{1}{2}$
Do. peroxide of, do.	2 Ditto + 1 do.	2
Chloric acid vapour	$1\frac{1}{2}$ Ditto + 1 do.	1
Do. ether do.	1 Olefiant gas + 1 chlorine	
Chlorocarbonic acid gas	1 Carbonic oxide + 1 do.	1
Chlorocyanic acid vapour	1 Cyanogen + 1 chlorine	2
Cyanogen gas	1 Nitrogen + 2 carbon	1
Ether, muriatic, vapour	1 Muriatic acid gas + 2 alcohol	2
Do. sulphuric do.	2 Olefiant gas + 1 aq. vapour	1
Fluoborate of ammonia	1 Fluoboric acid + 1 ammon.	(solid)
Do. sub- of do.	1 Ditto + 2 do.	ditto
Hydriodic acid gas	1 Hydrogen + 1 iodine	2
Hydrocyanic acid vapour	1 Cyanogen + 1 hydrogen	2
Iodic acid	$1\frac{1}{2}$ Oxygen + 1 iodine	
Muriatic acid gas	1 Hydrogen + 1 chlorine	2
Muriate of ammonia	1 Muriatic acid + 1 ammonia	(solid)
Nitric acid vapour	1 Nitrogen + $2\frac{1}{2}$ oxygen	1
Nitrous acid do.	1 Ditto + 2 do.	1
Hyponitrous do.	1 Ditto + $1\frac{1}{2}$ do.	1
Nitrous gas	1 Ditto + 1 do.	2
Do. oxide gas	1 Ditto + $\frac{1}{2}$ do.	1
Olefiant gas	2 Carbon + 2 hydrogen	1
Phosphureted hydrogen gas	$1\frac{1}{2}$ Hydrogen + 0.5 phosphorus	1
Biphosphureted do.	$1\frac{1}{2}$ Ditto + 0.75 do.	1
Sulphureted hydrogen gas	1 Sulphur + 1 hydrogen	1
Sulphurous acid do.	1 Ditto + 1 oxygen	1
Sulphuric acid vapour	2 Sulphurous acid + 1 oxygen	2
Sulphuret of carbon vapour	1 Carbon + 2 sulphur	2

*Number of Atoms in each Volume, supposing 1 Volume of Oxygen to represent an Atom.*

2 vols. hydrogen .. = 1 atom.  
 2 vols. chlorine .. = 1 atom.  
 2 vols. nitrogen .. = 1 atom.  
 2 vols. carbon .... = 1 atom.

2 vols. cyanogen .. = 1 atom.  
 1 vol. nitr. oxide = 1 atom.  
 2 vols. nitr. gas .. = 1 atom.  
 2 vols. ammonia .. = 1 atom.

*Table of the Quantity of Oil of Vitriol of Commerce (sp. gr. 1.8485), and of Dry Sulphuric Acid in 100 Parts by Weight of diluted Acid at different Densities. By DR. URE.*

(Quarterly Journal of Science, &c. iv. 122.)

Liquid	Sp. Gr.	Dry.	Liquid	Sp. Gr.	Dry.	Liquid	Sp. Gr.	Dry.
100	1.8485	81.54	66	1.5503	53.82	32	1.2334	26.09
99	1.8475	80.72	65	1.5390	53.00	31	1.2260	25.28
98	1.8460	79.90	64	1.5280	52.18	30	1.2184	24.46
97	1.8439	79.09	63	1.5170	51.37	29	1.2108	23.65
96	1.8410	78.28	62	1.5066	50.55	28	1.2032	22.83
95	1.8376	77.46	61	1.4960	49.74	27	1.1956	22.01
94	1.8336	76.65	60	1.4860	48.92	26	1.1876	21.20
93	1.8290	75.83	59	1.4760	48.11	25	1.1792	20.38
92	1.8233	75.02	58	1.4660	47.29	24	1.1706	19.57
91	1.8179	74.20	57	1.4560	46.48	23	1.1626	18.75
90	1.8115	73.39	56	1.4460	45.66	22	1.1549	17.94
89	1.8043	72.57	55	1.4360	44.85	21	1.1480	17.12
88	1.7962	71.75	54	1.4265	44.03	20	1.1410	16.31
87	1.7870	70.94	53	1.4170	43.22	19	1.1330	15.49
86	1.7774	70.12	52	1.4073	42.40	18	1.1246	14.68
85	1.7673	69.31	51	1.3977	41.58	17	1.1165	13.86
84	1.7570	68.49	50	1.3884	40.77	16	1.1090	13.05
83	1.7465	67.68	49	1.3788	39.95	15	1.1019	12.23
82	1.7360	66.86	48	1.3697	39.14	14	1.0053	11.41
81	1.7245	66.05	47	1.3612	38.32	13	1.0887	10.60
80	1.7120	65.23	46	1.3530	37.51	12	1.0809	9.78
79	1.6993	64.42	45	1.3440	36.69	11	1.0743	8.97
78	1.6870	63.60	44	1.3345	35.88	10	1.0682	8.15
77	1.6750	62.78	43	1.3255	35.06	9	1.0614	7.34
76	1.6630	61.97	42	1.3165	34.25	8	1.0543	6.52
75	1.6520	61.15	41	1.3080	33.43	7	1.0477	5.71
74	1.6415	60.34	40	1.2999	32.61	6	1.0405	4.89
73	1.6321	59.52	39	1.2913	31.80	5	1.0336	4.08
72	1.6204	58.71	38	1.2826	30.98	4	1.0268	3.26
71	1.6090	57.89	37	1.2740	30.17	3	1.0206	2.446
70	1.5975	57.08	36	1.2654	29.35	2	1.0140	1.63
69	1.5868	56.26	35	1.2572	28.54	1	1.0074	0.8154
68	1.5760	55.45	34	1.2490	27.72			
67	1.5648	54.63	33	1.2409	26.91			

*Table of Simple Affinity.*

This Table, it may be necessary to observe, does not express accurately the *comparative affinities* of bodies, but denotes merely the actual *order of decomposition*. A valuable Table of Elective Attractions, numerically represented by Dr. Young, may be found in the Phil. Trans. for 1809, or in Nicholson's Journal, 8vo. xxiii. 354. The length of the Table, and of the explanation which should accompany it, prevent me from giving it a place in this Appendix.

<p>OXYGEN. Metallic bases of the alkalis and earths Carbon Manganese Zinc Iron Tin Antimony Hydrogen Phosphorus Sulphur Arsenic Nitrogen Nickel Cobalt Copper Bismuth Caloric ? Mercury Silver Arsenious acid Nitric oxide Gold Platinum Carbonic oxide</p>	<p>Chrome Bismuth Lead Copper Tellurium Platinum Mercury Silver Gold</p> <hr/> <p>CARBON. Oxygen Iron Hydrogen</p> <hr/> <p>NITROGEN. Oxygen Sulphur ? Phosphorus Hydrogen</p> <hr/> <p>HYDROGEN. Oxygen Sulphur Carbon Phosphorus Nitrogen</p> <hr/> <p>SULPHUR. PHOSPHORUS? Potassa Soda Iron Copper Tin Lead Silver</p>	<p>Bismuth Antimony Mercury Arsenic Molybdena</p> <hr/> <p>POTASSA, SODA, AND AMMONIA. <i>Acids.</i> Sulphuric Nitric Muriatic Phosphoric Fluoric Oxalic Tartaric Arsenic Succinic Citric Lactic Benzoic Sulphurous Acetic Mucic Boracic Nitrous Carbonic Prussic Oil Water Sulphur</p> <hr/> <p>BARYTA. <i>Acids.</i> Sulphuric Oxalic Succinic Fluoric Phosphoric Mucic</p>	<p><i>Acids.</i> Nitric Muriatic Suberic Citric Tartaric Arsenic Lactic Benzoic Acetic Boracic Sulphurous Nitrous Carbonic Prussic Sulphur Phosphorus Water Fixed oils</p> <hr/> <p>STRONTIA. <i>Acids.</i> Sulphuric Phosphoric Oxalic Tartaric Fluoric Nitric Muriatic Succinic Acetic Arsenic Boracic Carbonic Water</p> <hr/> <p>LIME. <i>Acids.</i> Oxalic Sulphuric Tartaric</p>	<p><i>Acids.</i> Succinic Phosphoric Mucic Nitric Muriatic Suberic Fluoric Arsenic Lactic Citric Malic Benzoic Acetic Boracic Sulphurous Nitrous Carbonic Prussic Sulphur Phosphorus Water Fixed oil</p> <hr/> <p>MAGNESIA. <i>Acids.</i> Oxalic Phosphoric Sulphuric Fluoric Arsenic Mucic Succinic Nitric Muriatic Tartaric Citric Malic ? Lactic Benzoic Acetic Boracic Sulphurous</p>
<p>OXYGEN.* Titanium Manganese Zinc Iron Uranium Molybdenum Tungsten Cobalt Antimony Nickel Arsenic</p>				

\* Vauquelin, in drawing up the column of the table, showing the relative affinities of the metals for oxygen, adopts, as the measure of the strength of affinity, the difficulty with which their oxides are decomposed by heat.

<i>Acids.</i> Nitrous Carbonic Prussic Sulphur	Carbonic Ammonia	Mucic Oxalic Arsenic Tartaric Phosphoric Muriatic Sulphurous	Sulphuric Nitric Tartaric Phosphoric Fluoric Succinic Citric Acetic Prussic Fixed alkalis Ammonia Fixed oils Water	Lactic Acetic Boracic Prussic Ammonia
ALUMINA. <i>Acids.</i> Sulphuric Nitric Muriatic Oxalic Arsenic Fluoric Tartaric Succinic Mucic Citric Phosphoric Lactic Benzoic Acetic Boracic Sulphurous Nitrous Carbonic Prussic	OXIDE OF SILVER. Gallic acid Muriatic Oxalic Sulphuric Mucic Phosphoric Sulphurous Nitric Arsenic Fluoric Tartaric Citric Lactic Succinic Acetic Prussic Carbonic Ammonia	Nitric Fluoric Citric Malic Succinic Lactic Acetic Benzoic Boracic Prussic Carbonic Fixed oils Ammonia	OXIDE OF IRON. Gallic Oxalic Tartaric Camphoric Sulphuric Mucic Muriatic Nitric Phosphoric Arsenic Fluoric Succinic Citric Lactic Acetic Boracic Prussic Carbonic	OXIDE OF ZINC. Gallic Oxalic Sulphuric Muriatic Mucic Nitric Tartaric Phosphoric Citric Succinic Fluoric Arsenic Lactic Acetic Boracic Prussic Carbonic Fixed alkalis Ammonia
SILICA. Fluoric acid Potassa	OXIDE OF MERCURY. Gallic acid Muriatic Oxalic Succinic Arsenic Phosphoric Sulphuric Mucic Tartaric Citric Malic Sulphurous Nitric Fluoric Acetic Benzoic Boracic Prussic Carbonic	OXIDE OF COPPER. Gallic Oxalic Tartaric Muriatic Sulphuric Mucic Nitric Arsenic Phosphoric Succinic Fluoric Citric Lactic Acetic Boracic Prussic Carbonic	OXIDE OF TIN.† Gallic Muriatic Sulphuric Oxalic Tartaric Arsenic Phosphoric Nitric Succinic Fluoric Mucic Citric	OXIDE OF ANTIMONY. Gallic Muriatic Benzoic Oxalic Sulphuric Nitric Tartaric Mucic Phosphoric Citric Succinic Fluoric Arsenic Lactic Acetic Boracic Prussic Fixed alkalis Ammonia
OXIDE OF PLATINUM. GOLD.* Gallic acid Muriatic Nitric Sulphuric Arsenic Fluoric Tartaric Phosphoric Oxalic Citric Acetic Succinic Prussic	OXIDE OF LEAD. Gallic Sulphuric	OXIDE OF ARSENIC. Gallic Muriatic Oxalic		

\* Omitting the oxalic, citric, succinic, and carbonic; and adding sulphureted hydrogen after ammonia.

† Bergman places the tartaric before the muriatic.

SULPHURIC ACID. PRUSSIC.* Baryta Strontia Potassa Soda Lime Magnesia Ammonia Glucina Ytria Alumina Zirconia Metallic oxides	Strontia Lime Potassa Soda Ammonia Magnesia Glucina Alumina Zirconia Metallic oxides Silica	Glucina Alumina Zirconia Metallic oxides	Alumina Zirconia	Soda Baryta Ammonia Alumina Magnesia
	PHOSPHOROUS ACID.	FLUORIC ACID. BORACIC.   ARSENIC.§ TUNGSTIC.	OXALIC ACID. TARTARIC. CITRIC.†† Lime Baryta Strontia Magnesia Potassa Soda Ammonia Alumina Metallic oxide Water Alcohol	FIXED OIL. Lime Baryta Potassa Soda Magnesia Oxide of mercury Other metal- lic oxides Alumina
SULPHUROUS ACID. SUCCINIC.† Baryta Lime Potassa Soda Strontia Magnesia Ammonia Glucina Alumina Zirconia Metallic oxides	Lime Baryta Strontia Potassa Soda Ammonia Glucina Alumina Zirconia Metallic oxides	Lime Baryta Strontia Magnesia Potassa Soda Ammonia Glucina Alumina Zirconia Silica	BENZOIC ACID. White oxide of arsenic Potassa Soda Ammonia Baryta Lime Magnesia Alumina	ALCOHOL. Water Ether Volatile oil Alkaline sul- phurets
	NITRIC ACID. MURIATIC.§	ACETIC ACID. LACTIC. SUBERIC.**	Baryta Potassa Soda Strontia Lime Ammonia Magnesia Metallic oxides Glucina	SULPHURETED HYDROGEN. Baryta Potassa Soda Lime Ammonia Magnesia Zirconia
PHOSPHORIC ACID. CARBONIC.‡ Baryta	Baryta Potassa Soda Strontia Lime Magnesia Ammonia		CAMPHORIC ACID. Lime Potassa	

\* With the omission of all after ammonia.

† Ammonia should come before magnesia; and strontia, glucina, and zirconia should be omitted.

‡ Magnesia should stand above ammonia, and alumina and silica should be omitted.

§ Ammonia should stand above magnesia.

|| Silica should be omitted, and, instead of it, water and alcohol be inserted.

¶ Except silica.

\*\* With the omission of strontia, metallic oxides, glucina, and zirconia.

†† Zirconia after alumina.

## TABLE

*Showing the Composition of several of the principal Mineral Waters.*

[N. B. The temperature, when not expressed, is to be understood to be 49° or 50° Fahrenheit.]

## I. CARBONATED WATERS.

SELTZER. Bergman.		SPA. Bergman.	
In each wine pint.		Specific gravity 1.0010.	
In each wine pint.		In each wine pint.	
Carbonic acid . . . . .	17 cub. in.	Carbonic acid . . . . .	13 cub. in.
Specific gravity 1.0027.		Specific gravity 1.0024.	
Carbonate of soda . . . . .	4 grs.	Carbonate of soda . . . . .	1.5 gr.
— of magnesia . . . . .	5	— of magnesia . . . . .	4.5
— of lime . . . . .	3	— of lime . . . . .	1.5
Chloride of sodium . . . . .	17	Chloride of sodium . . . . .	0.2
	<hr/> 29	Oxide of iron . . . . .	0.6
			<hr/> 8.3
CARLSBAD (Temperature 165° Fahr.)		PYRMONT. Bergman.	
Berzelius.		Specific gravity 1.0024.	
In a wine pint.		In each wine pint.	
Carbonic acid . . . . .	5 cub. in.	Carbonic acid . . . . .	26 cub. in.
In 1000 parts by weight.		In 1000 parts by weight.	
Sulphate of soda . . . . .	2.58714 grs.	Carbonate of magnesia . . . . .	10. grs.
Carbonate of soda . . . . .	1.25200	— of lime . . . . .	4.5
Chloride of sodium . . . . .	1.04893	Sulphate of magnesia . . . . .	5.5
Carbonate of lime . . . . .	0.31219	— of lime . . . . .	8.5
Fluate of do. . . . .	0.00331	Chloride of sodium . . . . .	1.5
Phosphate of do. . . . .	0.00019	Oxide of iron . . . . .	0.6
Carbonate of strontia . . . . .	0.00097		<hr/> 30.6
— of magnesia . . . . .	0.18221		
Phosphate of alumina . . . . .	0.00034	POUGES. Hassenfratz.	
Carbonate of iron . . . . .	0.00424	In each wine pint.	
— of manganese, a trace		Carbonic acid . . . . .	30 cub. in.
Silica . . . . .	0.07504	Carbonate of soda . . . . .	10. grs.
	<hr/> 5.46656	— of magnesia . . . . .	1.2
		— of lime . . . . .	12.
		Chloride of sodium . . . . .	2.2
		Oxide of iron . . . . .	2.5
		Silica . . . . .	0.5
			<hr/> 28.4

## Composition of Mineral Waters,—Continued.

## II. SULPHURETED WATERS.

AIX LA CHAPELLE. Bergman.	
Temperature 143°.	
In each wine pint.	
Sulphureted hydrogen....	5.5 cub. in.
Carbonate of soda ..	12. grs.
of lime.....	4.75
Muriate of soda.....	5.
	<hr/> 21 75

CHELTENHAM, Sulphur Spring.	
Brande and Parkes.	
Specific gravity 1.0085.	
In each wine pint.	
Carbonic acid .....	1.5 cub. in.
Sulphureted hydrogen....	2.5
Sulphate of soda.....	23 5 grs.
of magnesia .....	5.
of lime .....	1.2
Muriate of soda.....	35.
Oxide of iron .....	0.3
	<hr/> 65.

LEAMINGTON, Sulphur Water.	
Scudamore.	
Specific gravity 1.0042.	
Sulphureted hydrogen, quantity not ascertained.	
In each pint.	
Muriate of soda .....	15. grs.
of lime .....	7.96
of magnesia.....	3.30
Sulphate of soda...	11.60
Oxide of iron .....	a trace.
	<hr/> 37.86

MOFFAT. Garnet.	
Nitrogen .....	0.5 cub. in.
Carbonic acid .....	0.6
Sulphureted hydrogen ..	1.2
Muriate of soda .....	4 5 grs.

HARROGATE WATER.	
<i>New Well, at the Crown Inn.</i>	
(West, Quart. Journ. xv. 82.)	
Specific gravity 1.01286 at 69°.	
One wine gallon contains	
Sulphureted hydrogen....	6.4 cub. in.
Carbonic acid.....	5.25
Azote .....	6.5
Carbureted hydrogen ....	4.65
	<hr/> 22.8

Also,	
Muriate of soda .....	735. grs.
of lime .....	71.5
of magnesia .....	43.
Bi-carbonate of soda .....	14.75
	<hr/> 864.25

<i>Old Well.</i>	
Sp. gr. 1.01324 at 60°.	
Sulphureted hydrogen..	14.0 cub. in.
Carbonic acid .....	4.25
Azotic gas.....	8.
Carbureted hydrogen ..	4.15
	<hr/> 30.4

Also,	
Muriate of soda.....	752.0 grs.
of lime .....	65.75
of magnesia.....	29.2
Bi-carbonate of soda.....	12.8
	<hr/> 859.75

## III. SALINE WATERS.

SEIDLITZ. Bergman.	
Specific gravity 1.0060.	
in a pint.	
Carbonate of magnesia ....	2.5
of lime .....	0.3
Sulphate of magnesia ....	180.
of lime .....	5.
Muriate of magnesia .....	4.5
	<hr/> 192.8

CHELTENHAM, pure saline. Parkes and Brande	
In each pint.	
Sulphate of soda .....	15.
of magnesia .....	11.
of lime .....	4.5
Muriate of soda.....	50.
	<hr/> 80.5



*Composition of Mineral Waters,—Continued.*

LEAMINGTON, saline. Scudamore.

Specific gravity 1.0119.

In a pint.

Muriate of soda.....	53.75
——— of lime.....	28.64
——— of magnesia.....	20.16
Sulphate of soda.....	7.83
Oxide of iron.....	a trace.
	<hr/>
	110.38

LEAMINGTON, Lord Aylesford's spring.  
Scudamore.

Specific gravity 1.0093.

In a pint.

Muriate of soda.....	12.25
——— of lime.....	28.24
——— of magnesia.....	5.22
Sulphate of soda.....	32.96
Oxide of iron.....	a trace.
	<hr/>
	78.67

BRISTOL. Carrick.

Temp. 74°. Specific gravity 1.00077.

In each pint.

Carbonic acid.....	3.5 cub. in.
Carbonate of lime.....	1.5 grs.
Sulphate of soda.....	1.5
——— of lime.....	1.5
Muriate of soda.....	0.5
——— of magnesia.....	1.
	<hr/>
	6.0

BATH. Phillips.

Temp. 109° to 117°. Sp. gr. 1.002.

In each pint.

Carbonic acid.....	1.2 cub. in.
Carbonate of lime.....	0.8
Sulphate of soda.....	1.4
——— of lime.....	9.3
Muriate of soda.....	3.4
Silica.....	0.2
Oxide of iron.....	a trace.
	<hr/>
	16.3

BATH. Solid contents. Scudamore.

Muriate of lime.....	1.2 grs.
——— of magnesia.....	1.6
Sulphate of lime.....	9.5
——— of soda.....	.9
Silica.....	.2
Oxide of iron.....	.01985
Loss, partly carb. of soda ..	.58015
	<hr/>
	14.

BUXTON. Scudamore.

Sp. gr. at 60°. 1.0006. Temp. 82°.

In a wine gallon.

Carbonic acid.....	1.5 cub. in.
Nitrogen.....	4.64
	<hr/>
Muriate of magnesia.....	.58 grs.
——— of soda.....	2.40
Sulphate of lime.....	.6
Carbonate of lime.....	10.40
Extractive and vegetable matter.....	} 0.50
Loss.....	0.52
	<hr/>
	15.

Or, according to Dr. Murray's views,

Sulphate of soda.....	0.63
Muriate of lime.....	0.57
——— of soda.....	1.80
——— of magnesia.....	0.58
Carbonate of lime.....	10.40
Extract and loss.....	1.02
	<hr/>
	15.00

MATLOCK BATH. Scudamore.

Temp. 68°. Sp. gr. 1.0003.

Free carbonic acid.

Muriates and } magnesia, lime, and  
sulphates of } soda?  
in very minute quantities not yet  
ascertained.

*Composition of Mineral Waters,—Continued.*

IV. CHALYBEATE WATERS.

TUNBRIDGE. Scudamore.

Specific gravity 1.0007.

In each gallon.

Muriate of soda .....	2.46
——— of lime .....	0.39
——— of magnesia .....	0.29
Sulphate of lime .....	1.41
Carbonate of lime .....	0.27
Oxide of iron .....	2.22
Traces of manganese, vege- } table fibre, silica, &c. . . }	0.44
Loss .....	0.13
	7.61

CHELTENHAM. Brande and Parkes.

Specific gravity 1 0092.

In a pint.

Carbonic acid .....	2.5 cub. in.
Carbonate of soda .....	0.5
Sulphate of soda .....	22.7
——— of magnesia .....	6.
——— of lime .....	2.5
Muriate of soda .....	41.3
Oxide of iron .....	0.6
	73.8

BRIGHTON. Marcet.

Specific gravity 1.00108.

Carbonic acid gas .....	2½ cub. in.
Sulphate of iron.....	1.80 grs.
——— of lime .....	4.09
Muriate of soda.....	1.53
——— of magnesia .....	0.75
Silica .....	0.14
Loss .....	0.19
	8.50

HARROGATE, Oddie's chalybeate.  
Scudamore.

Specific gravity 1.0053.

In each gallon.

Muriate of soda .....	300.4
——— of lime .....	22.
——— of magnesia .....	9.9
Sulphate of lime.....	1.86
Carbonate of do.....	6.7
——— of magnesia ....	0.8
Oxide of iron .....	2.40
Residue, chiefly silica ....	.40
	344.46

## ADDENDA.

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### *Specific Heat of Gases.*

THE researches of MM. de la Rive and Marcet, of which I have given a general view (vol. i. p. 163), have been since pursued and extended by them, in consequence of its having been objected that the quantities of gas, operated upon, were too small to be the subjects of sound deductions. In their early experiments, each gas was introduced into an exceedingly thin glass ball, blown at the extremity of a bent tube, the open end of which was immersed in quicksilver. The column of that fluid, which rose in the tube, determined, by its height, the greater or less pressure on the gas; and the smallest variations of temperature in the latter were exhibited by an increase or diminution of elastic force, rendering sensible the movement of the mercury. In this way, when the pressure on the gas was from 68 to 70 centimetres, it was easy to appreciate a difference of temperature not exceeding the 25th part of a centigrade degree. The glass ball was, in each instance, inclosed in a hollow sphere of thin sheet copper, blackened internally, of which it occupied the centre. The ball of copper, exhausted by the air-pump, was placed in a vessel of water, heated to a temperature constantly elevated to the same point above that of the atmosphere. The heat, therefore, arrived at the glass ball by radiation; and, all the circumstances being precisely similar for each gas, introduced in succession into the ball, the greater or less temperature, acquired by each during equal intervals, ought to represent their specific heats.

From the experimental results acquired in this way, it appeared that under the same circumstances, and during the same time, a given volume of any gas was heated so much the more, as it was submitted to a less pressure; proving that the specific heat of gases, under the same volume, is so much the less, as they are more rarefied. The experiments, however, were not sufficiently extended to enable the observers to lay down accurately the proportion between the elastic force of a gas, and its

capacity for caloric. They were chiefly intended to show that, as their apparatus was adequate to discover the differences of capacity, in the same gas variously compressed, it may be fairly considered competent to appreciate even small differences of capacity, inherent in different gases.

To obviate, however, the objections made to the limited scale of their first experiments, they substituted an apparatus similar in plan, but of considerably larger size; the glass ball being made capable of containing 6.176 grains of atmospheric air, equal to very nearly 20 cubic inches. By substituting a glass stopcock, they were enabled to extend their experiments to chlorine and sulphureted hydrogen gases. The temperatures, acquired by the gases, were measured, as before, by the increase of their elastic force.

From a series of experiments, made with every precaution that could be thought of to avoid error, on atmospheric air, carbonic acid, nitrous oxide, olefiant, sulphureted hydrogen, chlorine, and hydrogen gases, it appeared that equal volumes of all the gases, (with the exception of hydrogen, which is known to possess a greater conducting power,) acquired, at the end of the same interval, by exposure to a like heating cause, the same increase of elastic force, and consequently the same increase of temperature. The deviations from this law, at least, were too insignificant to throw doubts on its generality, and were commonly explicable by the circumstances of the experiment. The former conclusion, therefore, of these philosophers, *viz.*, *that all gases have the same specific heat*, remains, in their opinion, unimpeached, provided it be admitted that the apparatus employed is capable of furnishing accurate results. But, under the least favourable view of its fitness for that purpose, they argue that if the gases do, in fact, differ from each other as to their specific heats, the greatest difference between them cannot exceed one-tenth of the specific heat of any one gas. Nor are they disposed to admit that the equal increase of temperature in all gases, from a similar heating cause, may be explained by supposing that the conducting power is, in each of them, proportioned to its specific heat; for this consequence is at variance not only with their own observations, but with all anterior ones. When the conductivity of a gas, hydrogen for instance, is really a little greater than that of others, this certainly exerts an influence, but one which it is easy to appreciate. The more rapid propagation of

heat in hydrogen gas, so distinctly shown by their experiments, furnishes, they think, additional proof of the sensibility of their apparatus. (Ann. de Ch. et de Ph. March 1829.)

The results of the inquiries of MM. de la Rive and Marceat have drawn the attention of M. Dulong, who, in conjunction with the late M. Petit, had already illustrated this obscure field of chemical investigation. Admitting, with the candour which might be expected from so excellent a philosopher, the ingenuity of the means of research adopted by the chemists of Geneva, their skill in the use of their apparatus, and the general accuracy of their observations, M. Dulong is still disposed to differ from them as to their conclusions. These he considers to be unsound, from an error of reasoning not uncommon in scientific logic; that the phenomenon, taken as the measure of specific heats, is not a simple one, depending upon one cause, but upon several; and that the amount, to which each of these causes acts, has not been separately and distinctly ascertained. He does not admit that the cooling or heating power of elastic fluids depends *only* upon capacities for caloric; but conceives that it must necessarily have a connexion with the inequalities of mass existing, no doubt, in the ultimate particles of æriform fluids, from which it must result that unequal velocities will be communicated to those particles by the same impulse. This mobility of the particles of elastic fluids among each other may materially affect the velocities, with which gaseous bodies are heated or cooled, independently of their specific heats; and the mobility is itself controlled by accidental circumstances, such as the figure of the containing vessel, the density of the gas, &c. It is, therefore, the *conductibility of gases*, and not *their capacities for heat*, which may be considered quite apart from each other, that M. Dulong conceives to be established by the chemists of Geneva. He regards, also, as a greater objection to the mode of operating than the latter seem disposed to admit, that the heat absorbed or given out by the glass globe, destined to contain the gas, constitutes too great a fraction of the whole heat, lost or gained during the experiment, to afford accurate results; a source of fallacy extremely difficult to avoid in operating on elastic fluids.

The above is but a very brief view, and that of a part only, of the objections, advanced by M. Dulong, against the opinions

of MM. de la Rive and Marcet, in a memoir which, though unfinished, is of considerable length. It would be inexpedient to follow the author, in this place, into arguments of the same tendency, derived from the analogy of the propagation of sound through different gases, and through the same gases differently compressed; a property depending, like the communication of heat, upon the mobility of gaseous particles among each other. The tendency of the whole of his researches, while it has led him to observations of great interest to the theory of heat, points to the necessity of opening new and less difficult paths to a true knowledge of the capacities of gaseous bodies for caloric. The following laws may, he thinks, however, be safely and confidently deduced from known facts.

1st. That equal volumes of all elastic fluids, whether simple or compound, taken at the same temperature and under the same pressure, being compressed or dilated suddenly by the same fraction of their volume, disengage or absorb the same *absolute quantity of caloric*.

2d. That the variations of *temperature*, which result, are in the inverse proportion of their specific caloric, under a constant volume. (Ann. de Ch. et de Phys. June 1829.)

*Powers of different Kinds of Wood to conduct Heat, and Influence of the Direction of the Fibres on its Transmission.*

At p. 108, vol. i. I have given M. Despretz's recently-constructed Table of the Powers of different Substances to conduct Heat. The subject has been lately made more complete by a series of experiments of MM. de la Rive and Decandolle, on the conductivity of different kinds of wood, as well in the direction of their fibres as in a contrary sense. (Ann. de Ch. et de Ph. Jan. 1829.)

Six kinds of wood were submitted to experiment; in three of which the conductivity was examined, both in a longitudinal and transverse direction. Arranged in the order of their conducting powers (the best conductors being first mentioned), they were found to be the wild service (*cratægus aria*), walnut, oak, fir, poplar, all in the direction of the fibres; then walnut, oak, and fir, in the transverse direction, and finally cork.

The densest woods were in general found to be the best conductors; nevertheless, walnut is a better conductor than oak,

though specifically lighter. The following extract, from the Table given by the authors, shows the height of a thermometer, the bulb of which was distant about .8 of an inch from that of another, placed nearer the source of heat, both bulbs being let into cavities formed in the wood. For the convenience of comparison, the temperature of the thermometer No. 1, next to the source of heat, is taken at 100° centig.; and a correction is made for the temperature of the atmosphere.

	Height of the therm. No. 2. (The course of the heat being length- wise of the wood.)	Height of the therm. No. 2. (The heat moving transversely to the fibres of the wood.)
Wild service . . . .	54°.28	. . . . . 37°.59
Walnut . . . . .	53 .7	
Oak . . . . .	50 .5	. . . . . 28 .57
Fir . . . . .	47 .62	. . . . . 19 .6
Poplar . . . . .	42 .91	. . . . . 17 .5

From the foregoing Table it appears that the difference is not very great, as to the conducting powers of woods, cut in the same direction; but that there is a decided difference in sections of the same wood, cut longitudinally or transversely. In general, woods conduct heat most slowly in a direction crosswise to the fibres, and the more imperfectly any given wood conducts, the greater is the difference between its conductivity, considered relatively to the direction of its fibres. Data derived from the Table show, for instance, that the conducting power, longitudinally, being in each represented by 100,

In wild service wood it is transversely about	69
Oak . . . . .	60
Fir . . . . .	41

The curve formed by the heights of the thermometers, when five equidistant ones are employed in the same experiment, is a logarithmic one for good conductors, but not so regular for bad ones. At first, it decreases very fast, and then becomes almost parallel to the line of the abscisses. Nor do the experimental numbers express the conducting powers with perfect accuracy, but are to be considered as influenced by many circumstances; such as, the dimensions of the bodies, their radiating property, and other elements of calculation which ought to be taken into

account, when we would compare exactly the conductivity of woods with that of other substances.

The great difference, resulting from the position in which the ligneous layers are presented to caloric, may explain in part why trees preserve so nearly, in the interior of their trunks, the temperature of the soil whence they draw their nourishment. In the one direction, caloric is transmitted by the ascending fluids, and propagated through the solid tissue. But the little conductivity in a transverse sense presents an obstacle to an equalization of the temperature of the trunk, with that of the surrounding atmosphere, which may have a most beneficial effect in the economy of vegetation.

*On the Influence that Liquefaction exerts over the Volume and Dilatability of some Bodies ; by M. G. A. Erman.*

The bodies, submitted to experiment by M. Erman, were, 1st. The alloy, known at Berlin as that of M. Rose, sen<sup>r</sup>. (consisting of 2 parts bismuth, 1 lead, and 1 tin), and 2dly. Phosphorus.

From 32° to 95° Fahr. the changes of volume in the compound metal are nearly proportional to the temperatures. Above the latter degree, near to which is the maximum of volume, the dilatation is replaced by a contraction, which at first is very rapid, but the rate of which diminishes, till the heat rises to 130° Fahr., when the minimum of volume ensues. The dilatations, which next follow, begin very slowly, and increase gradually to 167°, the point at which the alloy liquefies. From that point to 176° the dilatation is still very considerable, but beyond the latter it reassumes a march, rigorously similar to that which was observed before the irregular oscillation of volume, that is to say, the same as from 32° to 95°. Prolonging, downwards to 32°, the dilatation observed beyond 176°, we obtain, for the primitive volume, the same value as by observation. From hence it is inferred, that the oscillation of volume (between 95° and 167°) has no influence upon the final volume after liquefaction.

When the ball of a thermometer tube is filled with the fused alloy, and the latter allowed to cool, long after the solidification of the metal, the bulb is burst, exhibiting an infinite number of small cracks. By experiments made for the purpose, it was found that the rupture took place when the temperature had descended to 104° Fahr. This apparent anomaly agrees evi-



dently with the march of volume already mentioned. For seeing that the metal becomes solid at 167°, and moulds itself, so to speak, upon the interior surface of the ball; seeing moreover that it acquires at 95° a volume equal to that which it has at its term of congelation; and adding to this the contraction of glass between 167° and 95°, it is evident that at a temperature approaching the latter degree, the diameter of the metallic sphere ought to surpass that of the cavity of the glass, which inevitably causes a rupture.

In solid phosphorus, the changes of volume are proportional to the temperature, with the exception of some irregularities, which are probably due to errors of observation. Liquefaction produces in phosphorus a sudden expansion, which is independent of changes of temperature. When liquefied, phosphorus dilates much more considerably than when solid; but its changes are still sensibly proportional to the temperature.

The data for the dilatibility of ice are derived from a memoir by M. Heinrich, who has shown that the cubic contraction corresponding to 212° Fahr. is ..... = 0.073536 while that of water is only ..... = 0.043859 The dilatibility of water is greater before liquefaction than afterwards.

The following Table gives a summary view of the principal facts respecting the dilatibility of water, of Rose's alloy, and of phosphorus:

Water.	Alloy $\left\{ \begin{array}{l} 2 \text{ bismuth.} \\ 1 \text{ lead.} \\ 1 \text{ tin.} \end{array} \right.$	Phosphorus.
1. Dilates by congelation.	1. Condenses by solidification.	1. Condenses by solidification.
2. Dilatibility <i>greater</i> after congelation than before.	2. Dilatibility sensibly equal before and after congelation.	2. Dilatibility <i>less</i> after than before solidification.
3. Arrives at a <i>minimum</i> of volume, while <i>liquid</i> .	3. Arrives at a <i>minimum</i> of volume, while <i>solid</i> .	3. No <i>minimum</i> exists.
4. The <i>vols. of liquid</i> , that would be indicated by the continued march of the dilatation of the solid, are <i>greater</i> than the results of observation.	4. The <i>vols. of liquid</i> , indicated by the continued march of the dilatation of the solid, are <i>equal</i> to the result of observation.	4. The <i>vols. of liquid</i> , indicated by the continued march of the dilatation of the solid, are <i>less</i> than the results of observation.

The results announced under the heads 2, and 4, appear to Mr. Erman more favourable to the atomic theory, than the

dilatations which were before generally received, for reasons which he has stated at length in the memoir. (Ann. de Ch. et de Ph. Feb. 1829.)

*Compounds of Carbon with Iodine and Bromine.*

The formation of two distinct compounds of carbon and iodine is now admitted by Serullas to take place in the circumstances, under which he supposed hydriodide of carbon to have been produced, an oversight first corrected by Mitscherlich. The description, given vol. i. p. 385, applies to the *periodide*.

The *protiodide* of carbon was obtained by Mitscherlich by distilling the periodide with an equal weight of bi-chloride of mercury.

Led by analogy, Serullas has succeeded in forming a *bromide of carbon* by causing bromine in excess (2 parts) to act on 1 part of periodide of carbon. At the same time there is formed a *sub-bromide of iodine*, characterized by the abundant separation of iodine, which takes place on adding caustic potassa.

The bromide of carbon resembles in its physical properties the protiodide, inasmuch as to have occasioned their being mistaken for each other, but the iodide is of a deeper red colour. Both are heavier than water, and have the same penetrating ethereal odour, and intensely sweet taste, even when largely diluted. They are alike deprived of colour when washed, with a view to their purification, with liquid potassa. A physical character, distinguishing the *bromide* from the *hydro-bromide* of carbon (i. 447), is, that the former becomes hard and crystalline at 32° Fahr.; the latter not till the temperature is reduced 10° or 14° still lower; while the protiodide of carbon remains fluid at the lowest temperature, to which it has been exposed.

Paper impregnated with bromide of carbon, and then dried, burns in the flame of an alcohol lamp, with reddish vapours of bromine. Protiodide of carbon, similarly decomposed, emits vapours of iodine, which, when absorbed by starch paste, evolve the characteristic blue colour. The hydro-bromide of carbon, under the same circumstances, burns with a feeble green flame, and with a formation of hydro-bromic acid.

Neither the bromide nor the protiodide of carbon, placed in contact with water, has any sensible action on that fluid; but each undergoes a slow decomposition, marked chiefly by the colour arising from the evolution of bromine or of iodine.

When an alcoholic solution of bromine is mingled with a solution of potassa in the same menstruum, the liquid becomes saccharine to the taste, and aromatic to the smell, owing, doubtless, to the formation of bromide of carbon, though it is not easy to exhibit that compound in quantity.

The protiodide of carbon, analyzed by combustion with oxide of copper for the carbon, and by nitrate of silver for the iodine (the latter being deduced from the iodate of silver), gave results, which accord nearly with 1 atom of iodine + 1 atom of carbon. The periodide appears to consist of 3 atoms of iodine + 2 atoms of carbon. Only one compound of bromine and carbon is yet known, constituted, probably, of an atom of each element.

The analogy between chlorine, iodine, and bromine, when closely examined, is extremely striking:

1st. In giving *three ethers*, the hydro-chloric, hydriodic, and hydro-bromic.

2. Chlorine and iodine agree together in uniting with carbon, both in binary proportion (1 atom + 1 atom), and in the proportion of 3 atoms of the two first respectively with 2 atoms of carbon. The relative proportions, in which bromine and carbon unite, will probably prove conformable to the same analogy.

3. We have compounds of carbureted hydrogen with bromine, agreeing as to their general properties, but not yet so perfectly investigated as to enable us to assign their atomic constitution (vol. i. p. 446). To these I have given the name of *hydro-bromides*, but perhaps they would have been better designated as *hydro-carburets* of chlorine, iodine, and bromine. This depends, however, on the view we may take of the mode in which the three elements are united. The most probable one, perhaps, is that which regards them as held together by the mutual attraction of the three elements. (Ann. de Chim. et de Phys. Nov. 1828.)

#### *Atomic Weights of Iodine and Bromine.*

To determine the atomic weight of iodine, M. Berzelius decomposes iodide of silver, prepared with the greatest attention to its purity. Chlorine, slowly passed over the pulverized iodide, at common temperatures, is absorbed without disengaging iodine; and the iodide, at first yellow, becomes white; but when gently heated, iodine escapes, and chloride of silver remains. Chloride of silver, melted in chlorine, absorbs a

quantity of the gas, sufficient to be appreciable by the balance after cooling. It is necessary, therefore, in order to expel any excess of chlorine, to pass atmospheric air over the fused chloride, till the odour of chlorine has ceased.

From data thus obtained, the number 789.145 was derived as the atomic weight of iodine on the scale of Berzelius, = 126.2632, 2 volumes of hydrogen being unity; the estimated weight of its vapour is 8.7011; and the density of hydriodic acid gas 4.4193.

The atomic weight of bromine had been determined by Balard to be between 466.3 and 471.45. Liebig, by dissolving a known weight of silver in nitric acid, and precipitating it by bromide of potassium, made it 470.55, = 75.238 on the hydrogen scale; and Berzelius, by acting with chlorine on bromide of silver, obtained 489.15 on his scale, = 78.264 hydrogen being 1. The density of the vapour of bromine is therefore 5.3933, and that of hydro-bromic acid gas 2.731. (Ann. de Ch. et de Ph. April 1829.)

#### *Composition of certain Bromides.*

The following statement of the compositions of some of the bromides is derived from the experiments of M. Henry, jun. of Paris. (Phil. Mag. Aug. 1829.)

	Metal.	Bromine.
Per-bromide of iron . . . . .	15.27	84.73
Bromide of magnesium . . . . .	7.760	92.240
———— calcium . . . . .	11.974?	89.026
———— barium . . . . .	31.75?	68.31
———— potassium . . . . .	26.548	73.452
———— sodium . . . . .	13.38	86.62
Proto-bromide of mercury . . . . .	57.36	42.64
Per-bromide of ditto . . . . .	59.47	46.53

#### *Combinations of Bromine with Arsenic, Bismuth, and Antimony.*

*Arsenic*, placed in contact with bromine, burns with a vivid light and great heat; and abundant vapours arise, which are almost colourless and transparent, and, on cooling, are condensed into long needles. To prepare *bromide of arsenic*, the pulverized metal must be added, by little at once, to bromine contained in a tubulated retort. The product is volatile, and may be purified by distillation. It is solid at 68° F., but between

that temperature and  $77^{\circ}$  becomes liquid, and is then transparent, and of a light yellow colour. It instantly decomposes water, with a formation of oxide of arsenic, and of hydrobromic acid. The oxide, remaining united with a little of the bromide, constitutes an *oxi-bromide*; the acid retains a little oxide of arsenic, which, being soluble, does not separate on the addition of water, as it does when the oxi-bromides have an insoluble oxide for their base. Its atomic constitution, derived from the experiments of its discoverer Serullas, appears to be 1 atom of bromine + 3 atoms of arsenic.

*Antimony* unites with bromine with similar phenomena, but gives a product which is less fusible and less volatile than bromide of arsenic, which it resembles, however, in atomic constitution.

*Bismuth* unites with bromine, but not, like the two first metals, by simple contact at common temperatures; nor is there any production of heat unless the bismuth is contaminated, as it often is, with arsenic. To effect the combination, powdered bismuth must be heated with a great excess of bromine in a long tube. Yellowish vapours arise and condense on the inside of the tube, which appear to be a *bromide of bismuth* with excess of bromine; at the bottom of the tube a steel-grey solid remains, not unlike iodine in its aspect.

*Oxi-bromides*.—The compounds of this class with bases of arsenic, antimony, or bismuth, though dried at a temperature of commencing decomposition, give water when more strongly heated. This water, Serullas suggests, may be *formed* by the conversion of the compound, viewed as a sub-hydrobromate, into water, and a quantity of bromide corresponding to the quantity of oxygen of the particular oxide which is in excess. MM. Gay Lussac, Thenard, and Chevreul, however, regard the facts as perfectly consistent with the existence of true oxi-bromides, analogous to the oxi-chlorides, for which the first-mentioned philosophers contended in opposition to Davy. (See vol. i. 237.) Under this point of view, the fact only adds another to the numerous instances of the tenaciousness, with which certain compounds retain water. (Ann. de Ch. et de Ph. July 1828.)

*Discovery of Iodine and Bromine in certain Salt-Springs and Mineral Waters in England.*

Dr. Daubeny, Professor of Chemistry at Oxford, has obtained

bromine in a separate state from one of the Cheshire brine-springs, and has fully satisfied himself of the existence of iodine in two or three; but the proportions he has not yet determined. He has found iodine also in the purgative waters of Cheltenham, Leamington, Gloucester, and Tewkesbury; while bromine is of still more frequent occurrence, and is perhaps entirely absent from none of the English springs which contain much common salt, except perhaps that of Droitwich. (Phil. Mag. and Ann. of Phil. Sept. 1829.) In the number of the same work for October, Mr. Murray claims the discovery of iodine in the waters of Cheltenham and Gloucester, and of iodine and bromine in the brine springs at Ingestrie, in Staffordshire.

*On Sulphurous Acid in its liquid Form.*

The condensation of sulphurous acid gas into a liquid, by the united effect of a reduced temperature and increased pressure, has been already described (vol. i. p. 414). In this state, beside the properties, which have been noticed by Mr. Faraday and M. Bussy, the liquid exhibits others which have been more recently observed by Prof. Aug. de la Rive. (An. de Ch. et de Ph. Ap. 1829.) The acid, submitted to the experiments of the latter, was procured from sulphate of mercury, and dried, as perfectly as possible, by receiving it into a flask, No. 1, surrounded by a freezing mixture, from which the gaseous portion passed through a tube filled with recently-fused chloride of calcium, into another flask, No. 2, cooled like the first; and finally into a third flask, No. 3, where, with the aid of slightly increased pressure, obtained by immersing a bent tube a little depth into mercury, the condensation was completed. The disengagement of gas having lasted eight or ten hours, the receivers, which had been closely luted, were detached. In the first were found white crystals, composed of sulphurous acid and water; in No. 2 and 3, liquid sulphurous acid, quite anhydrous. The latter portion could not be preserved except in glass bottles hermetically sealed, and constantly surrounded by a freezing mixture.

The *crystals* are of a pure white, have a fresh and rather agreeable taste, and compose thin plates, similar to those of hydrate of chlorine (vol. i. p. 231), which they resemble considerably in form. They continue solid at about 40° or 41° Fahr., but at this temperature they abandon a little of their gaseous ingredient; at a still higher, they lose about one-fifth of

their weight, and about four-fifths remain, which are mere water. In their proportion of water, they approach, therefore, very nearly, to the hydrate of chlorine; but to determine their constitution precisely, fresh experiments would be necessary.

The properties of the *liquid anhydrous acid* have been already described (i. 414). Availing himself of the intense cold which it produces, M. de la Rive examined the comparative powers of fluid and of frozen mercury to conduct electricity. The result was, that mercury has its conducting power sensibly increased by being solidified. The cold, produced by the volatilization of this acid, is far more intense than is required to freeze mercury; but M. Bussy did not succeed in attempting to congeal, by its means, either sulphuric ether or concentrated alcohol. The small crystals that form spontaneously in the liquid acid, when relieved from pressure, are not the pure acid, but the hydrate; and derive their water from the aqueous vapour diffused through the atmosphere.

Sulphurous acid, being perfectly anhydrous, presented an opportunity of extending the general analogy of the relation of acids to electricity. Sulphuric acid, within certain limits, conducts less perfectly the more it is concentrated. Bromine, a fluid which in some properties resembles acids, is a conductor only when water has been added to it; and iodine does not conduct until moistened with water. Anhydrous sulphurous acid was proved, by a very delicate apparatus, to be a perfect non-conductor of the galvanic current; but when a little water was added, a rapid decomposition took place; sulphur and hydrogen were deposited at the negative pole, and oxygen at the positive.

M. de la Rive endeavoured to compare, experimentally, the refractive power of the anhydrous liquid acid with that which ought to result from a calculation founded on the refractive power of the gas, as ascertained by M. Dulong (vol. i. p. 166), and on the comparative densities of the liquid and the gas. The theoretical result differed from that of experiment, probably owing, in part, to imperfect data. But on extending the comparison to the refractive powers of gaseous and liquid ammonia, and gaseous and liquid sulphureted hydrogen, a similar anomaly was found to exist. Supposing the data to be correct, it would follow, from these three examples, that the refractive power of a body, in passing from a liquid to an elastic state, diminishes

in a proportion much greater than that in which the densities decrease ; thus confirming other exceptions, before advanced by MM. Arago and Petit, to the Newtonian law, that, consistently with the theory of the emission of light, *the refractive power of bodies of the same nature, but of different densities, ought to be proportional to their density.*

#### *Phosphoric Acid.*

The facts observed by Mr. Clark and M. Engelhart (which I have suggested, p. 418, may belong to the same class of phenomena) appear to have struck M. Gay Lussac in the same point of view ; and he is, moreover, of opinion that the change of properties, effected in phosphate of soda by calcination, is due to that which the phosphoric acid itself undergoes by the same cause. Not only is the power of the uncombined acid to precipitate albumen acquired by calcination, but a phosphate, prepared by saturating soda with acid so calcined, throws down a white precipitate from nitrate of silver. Calcined phosphate of soda dissolved in water, precipitated by acetate of lead, and then decomposed by sulphureted hydrogen, yields phosphoric acid, which is a precipitant of albumen, and throws down a white sediment from nitrate of silver. The change, produced in phosphoric acid by calcination, is much more permanent in acid which is combined with a base, than in the free acid. (Ann. de Ch. et de Ph. July 1829.)

#### *Compounds of Phosphorus with Hydrogen.*

The section on these compounds (vol. i. p. 459) having been recomposed under circumstances of interrupted attention, a few errors have crept into the text, towards which I must request the reader's indulgence. In that section I have endeavoured to extract, from a mass of conflicting testimony, the most probable evidence of the two generally admitted species of phosphureted hydrogen gas, considering the third variety as of too doubtful existence to be reasoned upon as a definite compound. The experiments of Dumas, of which I have given an account, have been recently repeated by M. Buff, in the laboratory of M. Gay Lussac. So far as respects proto-phosphureted hydrogen, the results of Dumas were fully confirmed, especially that 100 volumes require 200 of oxygen gas for saturation. But in the combustion of per-phosphureted hydrogen with oxygen,



some differences were observed. This gas (containing from 13.5 to 14.5 per cent. of impurity), when heated in a graduated glass vessel, deposited phosphorus without any change of volume, and, though it lost its spontaneous inflammability, continued to be absorbable to the same amount by solution of sulphate of copper. Besides being decomposed by keeping, its composition appeared to be varied by the degree of heat used in its production, so that we can never be sure of having it twice alike. Heated in contact with copper, each volume expanded to 1.5; mixed with three volumes of carbonic acid it burned completely both with oxygen gas and with air, without leaving any trace of phosphorus. In the quantities of oxygen consumed by the combustion of a given volume, great and unaccountable variations were observed, the lowest being 204, and the highest 270 volumes of oxygen, to 100 of the per-phosphureted gas.

Both gases agree in giving 1.5 volume of hydrogen from each volume, when decomposed by antimony, zinc, potassium, or bi-chloride of mercury; as well as in being absorbable by sulphuric acid, sulphate of copper, and chloride of lime. The following Table, which I have compiled from various authorities, exhibits the two species in contrast with each other.

*Table of the Gaseous Compounds of Hydrogen and Phosphorus.*

NAMES.	Specific gravity.		Each vol. takes oxygen.	Product.	Each vol. contains vols. of		By weight consists of	
	By expt.	Calculated.			hyd.	phos.	hyd.	phos.
1. Proto-phosph <sup>d</sup> . hydr <sup>n</sup> gas ( <i>not spontaneously inflammable</i> ) ....	1.214	1.2067	2.	{ Phosph <sup>c</sup> acid..	1.5 + 0.5	1 + 10.5917		
			or 1.5	{ Phosph <sup>s</sup> acid..				
2. Per-phosphur <sup>d</sup> . hydr <sup>n</sup> gas ( <i>spontaneously inflammable</i> ) .....	1.761	1.7580	2.675	{ Phosph <sup>c</sup> acid..	1.5 + 0.75	1 + 15.8875		
			or 1.875	{ Phosph <sup>s</sup> acid..				

The following Tables are added for the better comparison of the composition of the phosphoric and phosphorous acids, as deducible from the two proportions of oxygen, with which each variety of phosphureted hydrogen unites.

*Results of the Combustion of the two Species of phosphureted Hydrogen Gas with Oxygen Gas.*

	= Vols. of hydr. phos.		For phospho- ric acid.	For phos- phorous acid.
8 vols. of proto-phos- phureted gas . . . . }	12 + 6	take oxygen	16	. . . . . 12
Deduct oxygen due to the hydrogen			6	. . . . . 6
Oxygen due to the phosphorus			10	. . . . . 6
8 vols. of per-phos- phureted gas . . }	12 + 9	take oxygen	21	. . . . . 15
Deduct oxygen due to the hydrogen			6	. . . . . 6
Oxygen due to the phosphorus			15	9

The results of the combustion of both gases conspire, therefore, if correct, to prove that the proportion of oxygen in the phosphoric acid is to that in the phosphorous as 10 to 6, or 15 to 9, which are the same proportions as 5 to 3.

From a review of the compounds of hydrogen and phosphorus, I am disposed, however, to abide by the opinion expressed vol. i. p. 465, that more facts are wanted to decide the constitution of these gases. The facility of obtaining the proto-phosphureted hydrogen in a state of purity, the uniformity of its composition when first evolved, its permanency when long kept, and its uniting constantly with the same proportion of oxygen, point out that gas as a true chemical compound. Whereas, the variable purity of the per-phosphureted species, its change of constitution by mere standing, and the uncertainty as to the proportion of oxygen required for its combustion, show an instability of composition, which is inconsistent with the characters of a true chemical compound.

The equivalent number for phosphorus, however, as derived from the composition of either species of phosphureted hydrogen, does not accord with the relative weight of that substance (viz. 12), deducible from its compounds with oxygen. The nearest approximation to the number attained by the latter method is 10.5917. Multiplied and more correct experiments will, it is to be hoped, reconcile these incongruities.

*Fuming Liquor of Boyle.*

There are a few circumstances respecting this compound, chiefly relating to its formation, which have been justly thought worthy of investigation by Gay Lussac. When prepared by distilling

equal parts of lime and sal ammoniac, with half a part of sulphur, M. Thenard admits that no azotic gas is evolved; that chloride of calcium and hypo-sulphite of lime are generated; and that it is the hydrogen of the muriatic acid, contained in the sal ammoniac, which, with the sulphur, produces sulphureted hydrogen. In examining the circumstances of its production, M. Gay Lussac determined that, using anhydrous lime, the fuming liquid was not accompanied by even the smallest evolution of azote. At first, pure ammonia came over; then, the hydro-sulphuret in white crystals, which resolved themselves into the fuming liquor. The residue in the retort consisted of chloride and sulphuret of calcium and sulphate of lime, without any trace of the sulphite or hypo-sulphite of that base. This will not be surprising if it be considered that the heat, during the process, is necessarily raised to an obscure red, a temperature at which the sulphites and hypo-sulphites would be completely changed into sulphates and sulphurets. It is, moreover, incontestable that the volatile alkali has not furnished the hydrogen, which has united with the sulphur. The most natural source of hydrogen is the muriatic acid; but yet water, though not essential as a source of that element, appears to influence the phenomena for the following reasons:

In substituting, for muriate of ammonia, the sulphate or phosphate of that base, we still obtain fuming liquor without evolving azote. In this case, the hydrogen of the sulphureted hydrogen must necessarily have been furnished by water. But, as a more direct proof, sulphuret of calcium mixed with sulphur and water, and distilled together, gave abundance of sulphureted hydrogen gas. The same product was obtained by distilling moistened sulphuret of barium without any addition of sulphur; and still better, by passing the vapour of water over the same sulphuret ignited in a tube, because that compound contains three proportions of sulphur. But with sulphuret of calcium, which exists in one proportion only, the addition of sulphur is quite necessary. Without this addition, water is not decomposed, for the effect requires the concurrence of a double affinity.

It follows, therefore, that in preparing the fuming liquor of Boyle, a part of the sulphureted hydrogen is generated by the hydrogen of the muriatic acid, but that the water, formed at first by the action of that acid on lime, at a low temperature, may again, in part, react upon the mixture of sulphur and sulphuret of calcium, and produce sulphate of lime and sul-

phureted hydrogen. It follows too from the above observations, that we may replace sal ammoniac by another ammoniacal salt, provided it is a hydrate, or if not a hydrate, that we add water. (Ann. de Ch. et de Ph. March 1829.)

*Action of the Metals on Inflammable Gases, by MM. Aug. de la Rive and Marcet.*

A new method had been proposed by M. Pleischl of giving to platinum the property of becoming incandescent in a current of hydrogen gas. It consists in moistening unsized paper with a solution of the muriate (chloride) of platinum, and drying it three times successively; in burning the paper, and collecting the ashes. These ashes contain platinum in a state singularly adapted to exhibit the phenomena in question, even when the temperature approaches — 4° Fahr., though it requires a rather longer exposure to the gas to produce the effect. At — 4° F., the platinum ceases to be ignited. Palladium similarly prepared glows at nearly the same temperature as platinum; gold requires about 122° of Fahr, and silver from 250° to 260° F. The purer the metals, the more quickly and effectually do they act; and platinum, when prepared in this manner, does not spoil by keeping, as it is apt to do in the usual spongy form.

Olefiant gas (MM. de la Rive and Marcet find), when directed upon platinum thus divided, renders it incandescent, provided the metal, at the outset, be heated to 212° F. Macaire attests that bi-hydruret of carbon has the same effect at common temperatures, but he does not state how he procured that gas, which it is extremely difficult to obtain pure. My own experiments on mixtures of oxygen and olefiant gas, confined in contact with the platinum sponge over mercury, and gradually heated, gave 480° Fahr. for the temperature at which decomposition takes place under those circumstances, and 555° for carbureted hydrogen. (Phil. Trans. 1824, p. 278.)

Sulphureted hydrogen gas ignites platinum and palladium, and catches fire if those metals have an initial temperature a little exceeding 212°. Sulphur is deposited upon the metals, which require therefore to be cleaned anew for each operation by nitric acid.

Oxide of carbon produces a glow in platinum heated to 176° F., and in palladium heated to 248° F.; but though this initial temperature is necessary to ignition, yet it is not so to the production of carbonic acid. In my experiments, conducted as above, a visible diminution of volume did not hap-

pen under  $300^{\circ}$  or  $310^{\circ}$  Fahr. The metals, which have thus caused the formation of carbonic acid, become less sensible to the action of hydrogen gas, especially palladium, which requires to be heated afresh in order to recover its igniting property. The carbonic acid appears to be absorbed by a little charcoal mingled with the prepared metals, and most abundantly with the palladium.

A current of hydrogen gas, directed upon prepared platinum *in vacuo*, does not raise its temperature in the slightest degree, showing that the incandescence, when it does happen, is not owing to any immediate action of the hydrogen upon the platinum, as Doebereiner supposed. But on admitting as much air as sustained a column of mercury only  $1\frac{1}{2}$  inch high, the issuing hydrogen produced its usual effect, though the oxygen amounted to only an eighteenth of its common proportion in atmospheric air.

Of the conclusions drawn by MM. de la Rive and Marcet, the only one not already derived from former experiments respects the cause of the phenomenon. It is that the high temperature, causing incandescence of the metal, is due to the caloric abandoned by the gaseous bodies when their volume is reduced by combination; for example, by hydrogen and oxygen gases when they form water, and by carbonic oxide and oxygen gases when converted into carbonic acid. (Ann. de Ch. et de Ph. Nov. 1828.)

#### *Decomposition of metallic Chlorides by Olefiant Gas.*

When dry olefiant gas is passed over *per-chloride of antimony* Wöhler has observed, that it is absorbed in great abundance, the liquid becoming hot and assuming a brown colour. On cooling, it deposits a mass of transparent crystals of the *protochloride* of antimony. The liquor has now lost its fuming property, and has acquired a strong odour of hydro-chloride of carbon. On distillation, that liquid appears in a condensed state at the bottom of the receiver, with a solution of protochloride of antimony in the same fluid floating over it. Treating the liquid by muriatic acid and afterwards by water, the hydro-chloride of carbon is obtained pure.

The red volatile *per-chloride* of chrome exhibits similar appearances with olefiant gas; but the heat evolved is sometimes sufficient to inflame the gas, and to produce green protoxide of chrome. A chloride of chromium appears to be produced,

analogous to the brown oxide (p. 69 of this volume); a fact which Wöhler conceives to be favourable to our viewing that oxide as a definite compound.

The per-chloride of tin, the chloride of sulphur, and the red per-iodide of mercury are not decomposed by olefiant gas, nor altered as to the proportion of their elements. The per-fluorides, on account of their acting on glass, have not been tried.

When gaseous per-chloride of chrome (chloro-chromic acid, p. 71) is passed into absolute alcohol, it is absorbed, the liquid becomes very hot, and commonly the entering bubbles catch fire with a white flame. Green protoxide is deposited, and the liquid assumes the odour of the compound of chlorine with olefiant gas; but no ether is separable by adding water. (Ann. de Ch. et de Ph. Jan. 1829.)

*On the Products obtained by the Action of Chlorine on certain Salts, &c.*

Professor Liebig, of Giessen, has recently examined, with his usual ability, the products obtained by acting with chlorine upon certain acids and salts; an investigation of considerable interest to the general principles of chemical science, and calculated to throw light on some unsettled topics of discussion. Among these is the question, which has been already lightly touched (vol. i. p. 237), respecting the existence of an acid with base of chlorine, distinguished from the *chloric* by an inferior degree of oxygenation. This acid, which, if established, would most properly be called the *chlorous*, is believed by Berzelius to be formed, when chlorine acts upon hydrated metallic oxides (hydrate of potassa, or hydrate of lime for instance). The resulting salts he considers as constituted of those bases + chlorous acid; whereas, according to the generally received view, they are compounds of the bases with chlorine itself. In the present state of the discussion, I am not aware of any argument demonstrative of either of those opinions. M. Liebig appears inclined to think that the evidence preponderates in favour of the view taken by Berzelius; for he observes, that it would be an anomaly, if chlorine were to displace any acid from its combination with a base; while it is perfectly agreeable to analogy that the displacement should be made by an acid, such as the chlorous is supposed to be. This argument cannot, it appears to me, be admitted to have any great weight, if we consider the weak affinity of potassa for both those acids.

In the liquid obtained by passing chlorine through solution of acetate of potassa, M. Liebig observed some peculiar properties. It had the same effect upon the tongue as deutoxide of hydrogen, but showed no mark of agreement with that fluid in chemical properties; nor was oxygen disengaged from it by heat. It yielded by distillation acetic acid, and very little chlorine; and was resolved, by concentration, into chloride of potassium and chlorate of potassa, in the manner described vol. i. p. 556. Nothing occurred to indicate the ultimate decomposition of the acetic acid, in any stage of the process.

A solution of chlorate of potassa in water, being charged with chlorine, had similar properties to those of a solution of chlorine in water merely. Acids caused no effervescence; by exposure to the air, and by heat, it lost its gas, and very slightly precipitated nitrate of silver.

The synthesis of the *chlorites* (taking for granted that they exist) gives no insight into their constitution. M. Liebig supposes that more light may be thrown upon that part of the subject, by the action of oxidable substances upon chlorites. Sulphuret of lead, or sulphuret of barium, are instantly transformed into sulphates by liquid *chlorite of lime*; and if the latter be free from any obvious excess of chlorine, there is neither escape of chlorine, nor separation of sulphur; and there remains in the liquor neither baryta nor lead. Now to convert an atom of sulphur into sulphuric acid, three atoms of oxygen are necessary; and to oxidize an atom of base, another atom of oxygen is required; in all, four atoms to each atom of sulphuret. Four atoms of oxygen then (and not three as M. Liebig calculates) will best agree with the constitution of chlorous acid. This, it is true, is the composition of the peroxide of chlorine, taking Sir H. Davy's results as correct; but the experiments of Count Stadion indicate rather, that the peroxide consists of 3 atoms of oxygen + 1 atom of chlorine. The following, therefore (admitting the existence of chlorous acid), is a view not inconsistent with analogy.

	Atoms of chlor.	+ . . . .	Atoms of oxyg.
Protoxide of chlorine . . . . .	1	+ . . . .	1
Peroxide of ditto . . . . .	1	+ . . . .	3
Chlorous acid . . . . .	1	+ . . . .	4
Chloric acid . . . . .	1	+ . . . .	5
Per-chloric acid . . . . .	1	+ . . . .	7

The whole series, however, of the combinations of chlorine

and oxygen, seems to me to invite research, in order to bring them within that law of multiple proportions, which has been ascertained to hold in so many other instances, where the evidence is of a more decided and tangible kind.

*Action of Chlorine on metallic Sulpho-cyanides.*

The *sulpho-cyanides* are to be distinguished from the compounds of sulpho-cyanic acid described vol. i. p. 486 (which, if its analysis be correct, would have been more properly termed *hydro-sulpho-cyanic acid*). The sulpho-cyanides are to be regarded as compounds of sulphuret of cyanogen with metals. M. Liebig has examined the effect of chlorine upon those with bases of silver, lead, and potassium, and has obtained some curious and valuable results.

Chlorine is rapidly and abundantly absorbed by *sulpho-cyanide of silver*; much heat is evolved; and the mass acquires a cinnabar-red colour. When it is submitted to distillation, chloride of sulphur escapes, and a yellowish red sublimate arises. The decomposition, however, is incomplete, and the sublimate is too inconsiderable in quantity, to serve for analysis.

The *sulpho-cyanide of lead* was formed by mingling the solutions of neutral acetate of lead and of sulpho-cyanide of potassium: no immediate precipitate ensued, but, after agitating the mixture for a few minutes, brilliant yellow crystals were deposited. When these were heated in a glass tube, they swelled in bulk, and yielded cyanogen and bi-sulphuret of carbon; sulphur sublimed; and there remained sulphuret of lead, of a perfectly metallic aspect. Heated with nitric acid, the salt was instantly transformed into crystalline sulphate of lead, without any excess of sulphur being apparent; but the liquid, which floated over the crystals, precipitated the salts of baryta and of lead.

The sulpho-cyanide of lead was shown to be constituted of

	By experiment.	By calculation.
Cyanide of sulphur .....	36.19	35.87
Lead .....	63.81	64.13

---

100.

By substituting sub-acetate of lead, a compound was obtained, which experiment showed to consist of

Sulpho-cyanide of lead .....	59.639	} = 74.958 lead.
Oxide of lead .....	40.361	



The two *sulpho-cyanides of lead*, decomposed by dry chlorine, gave even less of the red sublimate than the similar salt of silver, and yielded only chloride of sulphur, and per-chloride of cyanogen. The product, however, of the action of chlorine on sulpho-cyanide of potassium, afforded the red sublimate in quantity sufficient for analysis. It was proved to be a compound of cyanogen and sulphur; the proportion of the latter being greater than exists in the radicle of the sulpho-cyanic acid, *viz.*,

Sulphur . . . . .	57.05
Cyanogen . . . . .	42.95
	100.

The nearest atomic proportions are two atoms of sulphur to one of cyanogen. The sublimate might, therefore, be called *bi-sulphuret of cyanogen*, if it were proved to be a true compound; but it is considered by Liebig rather as holding sulphur in excess. Apart from this excess, it may probably be the radicle of the last-mentioned acid.

When sulpho-cyanic acid is exposed to the atmosphere, a yellow deposit takes place. This deposit may be obtained, more promptly and abundantly, by boiling a solution of hydro-sulpho-cyanate of potassa with nitric acid. M. Wöhler finds it to be a compound of sulphur with hydro-sulpho-cyanic acid, and proposes to distinguish it by prefixing the word *sulphureted* to the latter compound epithet.

*Sulpho-cyanide of potassium* is rapidly decomposed by diluted nitric acid, especially in the proportion of 1 of the salt, 3 water, and 2 or  $2\frac{1}{2}$  nitric acid. Its saturated watery solution absorbs chlorine with great avidity, and the yellow sulphureted acid, just described, is precipitated; but not if the solution be very dilute. Sulphuric acid is formed in both cases, but more copiously in the latter, where none of the yellow powder appears. The yellow precipitate stains the skin intensely, and is distinguishable by a train of characteristic properties, fully described by MM. Liebig and Wöhler. (Ann. de Ch. et de Ph. xli. 196.)

The yellow substance gave by analysis so nearly the same results as the radicle of the hydro-sulpho-cyanic acid (*viz.*, 55.09 sulphur + 44.91 cyanogen), that the two compounds, though procured in different ways, may be pronounced to be identical. Neither of them affords water in any proportion that can cause

hydrogen to be viewed as more than accidentally present. M. Liebig, therefore, gives it the name of *sulphuret of cyanogen*, or *radicle of the hydro-sulpho-cyanic acid*. This acid, then, is analogous to the hydriodic and hydro-sulphuric acids (sulphureted hydrogen), in being decomposed by chlorine and by nitric acid, as well as by air, with the precipitation, in all three cases, of its respective radicle.

The sulphuret of cyanogen, obtained by either of the foregoing processes, differs materially from the compound described by Lassaigne under the same epithet (vol. i. p. 499). In fact, the proportions of the elements appear to be reversed, the compound described by Liebig being composed of 2 atoms of sulphur + 1 atom cyanogen; and that discovered by Lassaigne, of 1 atom of sulphur + 2 atoms of cyanogen.

*Sulpho-cyanic ether*.—Liebig, by distilling together 1 part of sulpho-cyanide of potassium, 2 of sulphuric acid, and 3 of alcohol 80 per cent. pure, and washing the product with water, has produced a new and peculiar variety of ether. It has a strong odour of assafoetida, which adheres permanently to substances moistened with it; its taste is somewhat saccharine, and resembles that of peppermint; it dissolves in alcohol and in sulphuric ether; takes fire easily; and, in burning, emits fumes of sulphurous acid. Its boiling point is between  $150^{\circ}$  and  $160^{\circ}$  Fahr. The presence of hydro-sulpho-cyanic acid in it could not be discovered by the experiments made with that view. It appears to M. Liebig to be a compound of sulphuret of cyanogen with hydro-carbon; a view confirmed by the fact that sulphurous acid always accompanies its formation. It is not, therefore, at the expense of the water in the alcohol that the potassium of the sulpho-cyanide of that metal is oxidized, but in consequence of the decomposition of the sulphuric acid. (Ann. de Ch. et de Ph., June 1829.)

#### *Action of Chlorine on Cyanate of Silver, &c.*

This differs accordingly as we act upon the cyanate in a state of solution; upon the dry crystals; or upon the crystals a little humid. In the latter case, the acid, described by Serullas (see vol. i. p. 482), is formed, and may be obtained in brilliant white crystals. In one or two instances, a white flocculent substance was obtained, supposed to be a compound of 2 atoms of cyanogen with 3 of chlorine. The existence of two ox-acids

with base of cyanogen, the cyanous and cyanic, is confirmed by these experiments.

Chlorine brought into contact with *fulminating silver*, mixed with water into a pulpy mass, affords a yellow heavy oily liquid, of an almost insupportable smell, and of a sweet yet burning taste, and which almost paralyzes the tongue. This is the perchloride of cyanogen described vol. i. p. 484.

Uric acid, moistened with water, is decomposed by chlorine; and oxalic acid, as is well known, is one of the products. This favours the presumption that uric acid is a compound of oxalic acid with some organized compound, possibly cyanic acid and ammonia.

Crystallized oxalic acid, and dry cyanite of potassa, rubbed together, develop an odour of hydro-cyanic acid, which soon yields to the more penetrating one of cyanous acid, and carbonic acid is also formed. When water is poured upon the residuum, a white flocculent substance remains, which shows a considerable agreement of properties with cystic oxide.

The powdered cyanate of potassa is converted by strong acetic acid, with phenomena described in the memoir, into crystals of cyanate of potassa.

*Purpuric acid*, Liebig is of opinion, may be considered as a combination of cyanic acid; and *uric acid*, of cyanous acid, with hydrogen. The pyro-uric acid, he finds (as Wöhler had also ascertained) is identical with the cyanic.

*Tartaric, acetic, and benzoic acids*, are scarcely attacked by chlorine. The acetic acid alone appears to undergo any change. It acquires a penetrating odour, and emits vapours which painfully affect the eyes. It becomes, too, capable of precipitating perchloride of iron of a brownish red.

*Sugar, gum, and starch*, in solution, are not easily acted upon by chlorine gas, even when passed through them during eight hours. The only products are carbonic and hydrochloric acids. The same substances, in a dry state, exhibit scarcely any signs of decomposition.

Perfectly pure *prussian blue*, heated with a solution of chlorite of lime, is decomposed rapidly, with a disengagement of cyanogen or cyanic acid; the liquid becomes reddish brown, and precipitates salts of peroxide of iron of a deep blue. By evaporation, we obtain crystals of chlorate of potassa, and the double salt of percyanide of iron with cyanide of calcium. The

presence of chlorate of potassa proves that prussian blue, even the purest, contains that alkali. (Ann. de Ch. et de Ph., July 1829.)

*Action of Chlorine on Ferro-cyanate of Potassa.*

It is asserted by M. Robiquet, in the Journ. de Pharm., that in converting ferro-cyanate of potassa into the red salt described by Mr. Johnston (vol. i. p. 576), a quantity of chloride of potassium is formed. If this be the case, the acid, alluded to p. 577, will contain no chlorine, nor will any of the salts. The question will probably be re-examined by Mr. Johnston.

M. Girardin obtains the red ferro-cyanate of potassa, by passing chlorine gas into a moderately strong solution of the common ferro-cyanate, until the solution ceases to produce any effect upon adding a portion of it to a solution of peroxide of iron. The liquid is then concentrated to two-thirds of its volume, and set aside in a moderately warm stove to crystallize. After some time, yellow, brilliant, and slender crystals are obtained, in the form of roses; by a second crystallization, very long needle-shaped crystals appear in tufts. The latter are ruby-coloured, transparent, and very brilliant; their form appears to be an elongated octahedron. The principal character of this salt is that it precipitates the protosalts of iron blue or green, according to the proportion in solution; but, on the contrary, it does not precipitate the salts with base of peroxide of that metal. It is a most delicate test of protoxide of iron, detecting 1-90,000th part of that oxide, while common ferro-cyanate does not discover less than 1-1800th part.

The red ferro-cyanate of potassa is soluble in twice its weight of cold water, and in less than its weight of boiling water. It is insoluble in alcohol, does not act upon litmus, but renders syrup of violets green. The concentrated solution in large quantity is almost black, its colour being extremely deep; but in small portions it is transparent, and of a greenish red colour. A very small portion renders a large quantity of water green. In the formation of this salt, half the acid of the ferro-cyanate is destroyed by the chlorine, and the alkali of this half combines with chlorine. The ferro-cyanates of soda, ammonia, baryta, and lime, are all converted into red ferro-cyanates by chlorine. (Phil. Mag. and Ann. of Phil. v. 148.)

*On Jelly and Pectic Acid, and the Analysis of the Root of the Carrot.*

This useful vegetable has been recently submitted to experiment by M. Vauquelin, a philosopher distinguished not less by the long duration, than by the number and value, of his labours in chemical science.

I. From the root of the carrot, reduced into a pulp by rasping, a juice may be obtained by pressure, which is not quite transparent, has a sweet taste, a peculiar odour, reddens feebly tincture of litmus, and yields an abundant precipitate on adding acetate of lead. The precipitate, being first well washed, and then decomposed by sulphureted hydrogen, affords no vegetable acid except the *malic*.

II. 1. Evaporated to dryness, and then burned, the recently expressed liquor of the carrot is found to contain lime and potash, united with phosphoric, muriatic, and carbonic acids, the last-mentioned probably being the result of combustion. 2. At the temperature of 212° Faht., the juice is coagulated, and flakes of albumen separate, which, when collected and washed on a filter, have a yellow colour, and a characteristic odour, and therefore cannot be considered as pure albumen. 3. Alcohol, by digestion, extracts from these flakes, 1st, a fatty resinoid substance, of a semi-fluid consistence, evidently itself a compound. In this reside the colour, taste, and odour of the root; and, as it is not soluble in water, its suspension in the juice must be ascribed to the mediation of the albumen and saccharine matter. A further portion of this substance may be extracted by alcohol from the *marc* (pressed mass) of the carrot. 4. The albuminous flakes, after being acted upon in succession by alcohol and ether, are deprived of colour, and assume all the physical and chemical characters of coagulated albumen. 5. The alcoholic liquor affords, also, needle-shaped crystals, having all the properties of *mannite* (a peculiar kind of saccharine matter, which crystallizes during cooling from a solution of manna in heated alcohol).

III. The juice of carrots, cleared by coagulation and filtration, is amber coloured, and has a decidedly sweet taste. 1. When inspissated by evaporation, it yields a brown viscid mass, not wholly soluble, even in a large quantity of pure alcohol. 2. That fluid, nevertheless, acquires an amber tinge, and extracts a little saccharine matter, obtainable by evaporation

in a thick state not unlike molasses, of an agreeable and somewhat acid flavour, and not susceptible of crystallization. 3. This saccharine matter, placed under fit circumstances, passed through the vinous fermentation, and afforded alcohol.

IV. The portion of extract, which resisted the action of pure alcohol, was partially soluble in that fluid, reduced to the sp. gr. .897. The solution, being evaporated, left a product sensibly sweet, which gave azote by destructive distillation. It appears then to be constituted of (1) sugar, combined with (2) an azotized fermentable principle, from which no method has been found of separating it. (3) By using alcohol, progressively weaker and weaker, we obtain at length a white precipitate in considerable quantity, altogether insoluble in water, even when heated. This is partially soluble in weak acids, and in dilute alkalis, forming gelatinous solutions. By ultimate decomposition *per se*, it yields no ammonia, but gives penetrating fumes, resembling those which arise from gum similarly treated. Though insoluble in water, it appears to be held dissolved in the juice of the carrot, by the intervention of sugar, which is itself combined with sufficient force to resist the usual solvent action of alcohol.

V. When the juice of carrots, strained after boiling, is kept for a few days at the temperature of the atmosphere, it acquires a slight odour of vinegar, and a consistency nearly resembling white of egg. Arrived at this state, it appears remarkably indisposed to further decomposition, and may be kept two or three months at least, without any increase of acidity or further change. This passive state appears to be owing to the presence of the matter (IV. 3.) separately insoluble in water, but held in solution by the sugar; for, when deprived of its sugar by strong alcohol, and then boiled and strained, the juice becomes readily susceptible of the vinous fermentation. It is the presence of the same principle that seems to determine the production of *mannite*, which is confined to the compound fluid, and does not take place if the sugar be first isolated, and then dissolved in water.

VI. From the juice of carrots, altered by keeping, pure alcohol throws down abundant gelatinous flakes, not exactly similar in external characters to the insoluble substance left by weak alcohol, (IV. 3.) but in chemical properties identically the same. The alcoholic liquor yields, by evaporation, crystals of

*mannite*. The insoluble substance (IV. 3,) M. Vauquelin apprehends, is present in most vegetable juices that become ropery by keeping; and this property he ascribes to the spontaneous decomposition of the sugar, which formed originally a soluble compound with the substance occasioning the ropiness.

The *marc*, or solid which remains under the press, contains vegetable fibrin, and pectic acid. The residuum of its combustion affords phosphate and carbonate of lime. The pectic acid (which has been also recognized by Berzelius as a distinct and peculiar compound,) when heated in a crucible with excess of potassa, furnishes oxalic acid. In obtaining pectic acid, Vauquelin finds that ordinary spring water may be employed, if we substitute, for a caustic alkali, an equivalent quantity of its carbonate, which has, besides, the advantages of greater facility in practice, and of affording a purer product. (Ann. de Ch. et de Ph., May 1829.)

*Action of Litharge (Protoxide of Lead) on Metallic Sulphurets.*

Berthier has examined, with his usual sagacity, the results of this mutual action, which derive additional interest from the light thrown by them on the constitution and habitudes of sulphurets. Without following him through the details, which are nevertheless deserving the attention of the more advanced students of chemistry, I shall confine myself to a brief view of the general tendency of his experiments.

Litharge exercises a vivid action upon all the sulphurets, even at a temperature not much elevated. If the oxide is used in sufficient quantity, the sulphuret is decomposed entirely. Most commonly the sulphur is disengaged in the state of sulphurous acid gas, and the metal remains either alloyed with the lead which is reduced, or combined, as an oxide, with the portion of litharge which has not been decomposed. The quantity of litharge, which is required, varies for different sulphurets. For complete decomposition it is considerable, in some instances not less than thirty times the weight of the sulphuret being necessary. When less litharge is used than is essential to the full effect, a part only of the sulphuret is acted upon: this reduces a corresponding portion of the oxide of lead. The remainder of the sulphuret and of the oxide form, together with the new metallic oxide, which has been generated, a very

fusible combination belonging to the class of *oxi-sulphurets*, the existence of which I have stated to be somewhat doubtful. (See vol. i. p. 531.) The oxide of lead and the sulphurets are so strongly united in compounds of this sort, that galena (sulphuret of lead), which is easily attacked by pure litharge, cannot detach the smallest portion of lead from an oxisulphuret, provided the latter be fully saturated with sulphuret, and that the sulphuret in this compound continue unaltered as to its constitution.

When we treat a sulphuret with a less proportion of litharge, we form sulphuret of lead, which combines either with the portion of the metallic sulphuret which is not decomposed, or with an oxisulphuret. In this case, both the constituents of litharge, lead, and oxygen, contribute to desulphurize the metal.

Many oxides, also, in uniting with oxide of lead, considerably diminish the decomposing power of that oxide over metallic sulphurets. When we heat litharge with a sulphuret, the action of the former on the latter is limited by the affinity of the portion of sulphuret which enters into combination with it, as well as by the affinity of the metallic oxide which results from the portion of sulphuret that has been decomposed. But, in adding to any oxisulphuret a due dose of litharge, we may always decompose entirely the sulphuret which it contains.

When the sulphurets have powerful bases, as those of the metals of the alkalis and earths for example, no sulphurous acid is formed with litharge, but it converts all the sulphur into sulphuric acid. (Ann. de Ch. et de Ph. Nov. 1828.)

*Specific Gravities of Alloys, and their points of fusion.*

M. Kupffer, by former experiments on the *alloys of tin and lead*, had confirmed the common result, that those alloys have a less specific gravity, than the mean, calculated from the specific gravities of their components. They dilate therefore by combination; and the amount of this dilatation attains its *minimum*, when the combining proportions are two atoms of tin to one atom of lead. Lately, he has found that the *amalgams* of tin also experience a contraction, which diminishes if we begin with a compound of two atoms of tin and one of mercury, and proceed by degrees to an amalgam, in which those proportions are reversed, when it finishes by being exceedingly small. Augmenting the number of atoms of mercury, the contraction begins



anew; so that in an amalgam of one atom of tin and three of mercury, the contraction is almost as great, as in that of a compound, consisting of one atom of each metal. It seemed probable, then, that between the proportions of one atom of tin to two atoms of mercury, and of one atom of the former to three of the latter, there should be a proportion where no contraction would be observed. In prosecuting this inquiry, it was found that the alloys of tin and lead possess the same property; that is to say, that those metals may always be combined in such proportions, that there shall be neither a sensible contraction nor expansion; and that then the proportions of their elements are to their specific gravities in a very simple relation.

The researches of M. Kupffer appear to have been made with great care, and with delicate instruments. The results are exhibited in a series of tables. From experiments on tin and lead, he had reason to believe that the alloy, in which those metals combine without either expansion or contraction of elements, is obtained by uniting one volume of lead to two volumes of tin, proportions very nearly half way between two atoms of tin to one atom of lead, and three atoms of tin to one atom of lead.

Tin and mercury, in general, exhibit a great contraction by their union; but this contraction ceases when one volume of tin is united with two volumes of mercury. The actual sp. gr. of an amalgam of mercury and tin is nearest to the calculated sp. gr. when one vol. of tin is united with three vols of mercury.

It is remarkable that the actual dilatation, which all the above alloys and amalgams undergo by being heated, is less than it ought to be, supposing each metal to preserve its peculiar dilatability. It follows then that the approximation of the molecules increases the resistance, which their mutual attraction opposes to the expansive effect of heat.

In the course of his inquiries, M. Kupffer had occasion to take the fusing point of several alloys with considerable accuracy. The results, after being corrected by the experiments of Dulong, were as follow. The numbers, prefixed to the metals, represent atoms.

	Fusing point.		Fusing point.
Lead (sp. gr. 11.3303)	632 Fah.	3 tin + 1 lead ..	366.8 Fah.
Tin (sp. gr. 7.2911)	446 do.	2 tin + 1 lead ..	384.8 do.
5 tin + 1 lead . . . .	381.2 do.	1 tin + 1 lead ..	465.8 do.
4 tin + 1 lead . . . .	372.2 do.	1 tin + 3 lead ..	5.522 do.
One vol. lead + two vols. tin fused at 381.2.			

The atomic weights of the several metals, assumed in regulating the proportions, are not stated. Most probably they were adopted from the table of Berzelius; and these, reduced to the scale, in which 2 vols. of hydrogen are unity, correspond with 58.9195 for tin, 103.729 for lead, and 202.8625 for mercury.

*Distinctive Characters between Potassium and Sodium.*

A fragment of potassium, placed on the surface of mercury, exhibits, during its amalgamation, a rapid whirling motion. This depends on its strong action on the aqueous vapour of the atmosphere, and on the consequent emission of hydrogen gas; for, in air artificially dried, the potassium is amalgamated without motion. Sodium, on the contrary, if thrown upon the surface of quicksilver, is forcibly projected off it, with great heat and light, as originally observed by Gay Lussac and Thenard.

Potassium, it is well known, inflames on contact with water, while sodium decomposes water without combustion. These characters, then, may be employed to discriminate the two metalloids, since each possesses them in a precisely inverse order. In the case of potassium, the temperature, produced by its action on water, amounts to incandescence; whereas sodium does not excite heat enough for its inflammation. But if a fragment of the latter metal be thrown upon mucilage of gum arabic, of sufficient but not of too great spissitude, it then enters into ignition, and traverses the surface of the liquid. The flame is yellowish, not blue like that of potassium. Water does not produce the combustion of sodium, because it conducts the evolved caloric away too rapidly. But if the sodium be laid on a bad conductor, (wood, for instance,) and touched with a drop of water, it instantly takes fire. (Sérullas, An. de Ch. et de Ph. Mar. 1829.)

*Borate of Soda (Borax).*

A method of analyzing (or rather assaying) borax, has been contrived by M. Gay Lussac, (An. de Ch. et de Ph. xl. 398,) which he finds more practicable than that of Arfwedson, though not superior to it in correctness. It consists in determining, by successive additions of known quantities of sulphuric acid, the quantity of soda, and of course of borax, in any specimen of the salt. For though the disengaged boracic acid reddens litmus, yet the colour which it produces is a wine-red, while sulphuric acid evolves a tint resembling that of the peel of the onion.

The process of M. Gay Lussac is executed, he observes, as speedily and correctly as an alkalimetric assay; for the slightest excess of sulphuric acid, above what is necessary to saturate the alkaline base of the borax, is instantly evidenced by the difference of shade in the red colour. To attain precision, however, attention is necessary to several little details. Some of the directions it would be useless to copy, because they are adapted to the sulphuric acid manufactured in France, the specific gravity of which is not stated. The chief precaution is to reserve about one-tenth (as nearly as can be estimated before-hand) of the sulphuric acid, till the solution of borax has, by cooling, deposited much of the free boracic acid, which would interfere with the distinctness of the effect. This effect will be rendered still more nicely appreciable, by comparison with an infusion of litmus of like strength, coloured by a drop or two of diluted sulphuric acid. When rigorous accuracy is required, it is necessary to deduct from the total quantity of diluted sulphuric acid the few last drops, which have given a decided tint to the colour-test.

The proportion of real sulphuric acid required to decompose 100 grains, or any other definite quantity, of borax, may be learned at once from the atomic constitution of that salt (i. 590). From the Table of the Strength of Sulphuric Acid of different Densities (p. 671), it is easy to know how much diluted acid of any specific gravity must be taken as equivalent to the real acid required. This quantity of diluted acid, being completely mixed with as much water as will make up 100 (or 1000) aliquot measures of any denomination, may be added gradually to the solution of borax, till the requisite effect is produced on the colour-test. The proportion of the acid liquor actually expended, read off from the scale of aliquot parts, which ought to be engraved on the measuring tube, will indicate at once the per-centage of borate of soda. The whole operation, indeed, is precisely analogous to that of various other assays; the principle of which is to act, with all possible care, upon a known quantity of the subject of experiment *a*, with a known quantity of another substance *b*, which is capable of producing complete neutralization in *a*; and then, by weighing or measuring the remainder (if any) of *b*, to ascertain how much has been spent in producing the required effect on the coloured test-liquors. In the foregoing case, it is easy, from the quantity of test-acid actually expended, to

deduce the quantity of borax decomposed; for as 40 (grains of real sulphuric acid) are to 152 (of borax), so are the grains of real sulphuric acid spent in the assay to the number required. If the whole equivalent quantity of sulphuric acid has been found necessary, the complete purity of the borax, provided the specimen contains only its proper elements, may be considered as proved. The application of the same principle to the determination of the strength of chlorides is the subject of a memoir of M. Gay Lussac, (see vol. i. p. 609,) and that of alkalis is treated of in a recent essay by the same author, printed in the *Ann. de Ch. et de Ph.* Dec. 1828.

#### *Factitious Ultramarine.*

A combination of silica with alumina is the basis of the factitious *ultramarine*, for the preparation of which the following process has been given by Professor Gmelin, of Tübingen:

1. Prepare hydrate of silica, by fusing finely pulverized quartz with four times its weight of (sub) carbonate of potassa; dissolving the fused mass in water; and precipitating by muriatic acid. Prepare, also, hydrate of alumina, by precipitating a solution of alum with ammonia. These two precipitates are to be carefully washed with distilled water, drained, and a portion of each dried and ignited, to determine how much water each of the substances contains. In Gmelin's experiments, the hydrate of silica contained in 100 parts 56, and the hydrate of alumina 3.24, of dry earth.

2. Dissolve, afterwards, as much of the hydrate of silica as a heated solution of caustic soda is capable of taking up; and ascertain how much of the hydrate has been dissolved. For 72 parts of anhydrous silica, take a quantity of alumina equivalent to 70 parts, supposed anhydrous. Add this to the solution of silica, and evaporate, stirring constantly, till a moist powder only remains.

3. Into a Hessian crucible, provided with a good cover, put a mixture of two parts of sulphur and one part of dry carbonate of soda, and gradually heat till the mass is well fused. The mixture of the hydrated earths and soda (2) is then to be projected, by very small quantities, into the middle of the fused mass; vapour escapes in great quantity; and this is to be allowed to cease every time, before throwing in a fresh quantity. Having kept the crucible moderately red-hot for an hour, it is to be taken

from the fire, and allowed to cool. It now contains *ultramarine*, mixed with an excess of sulphuret, which is to be separated by water. If sulphur be in excess, it is to be expelled by a moderate heat. If the whole of the ultramarine be not equally coloured, the finer parts may be separated, after having reduced them to powder, by washing with water. (Ann. de Ch. et de Ph. April 1828.)

M. Kuhlman has since observed that a substance analogous to ultramarine is formed, when sulphate of soda is calcined in a reverberatory furnace. In this case, the production of sulphuret of sodium is probably the first step in the process. (Ann. de Ch. April 1829.)

#### *Indigotic Acid.*

This acid, of which I have given a short notice (p. 306 of this vol.), M. Buff finds may be produced without difficulty by the process there described. It may be separated, in part, from the resinous matter accompanying it, by pressure; after which it is to be dried in a water-bath, in order to expel the redundant nitric acid. From the residue, warm water readily extracts the indigotic acid. The solution is then saturated with fresh precipitated carbonate of lead, added in successive portions, until the effervescence, which is at first very brisk, begins to slacken, and the liquor to lose its transparency. At this point the additions must cease; for, if continued, an insoluble sub-salt of lead is produced. The liquor being poured into a shallow vessel, all the remaining impurities soon separate, and we obtain *indigotate of lead*, from which the base may be detached by a due proportion of sulphuric acid.

The recent experiments of M. Buff were directed principally to the analysis of this acid, which was effected circuitously by converting it into carbazotic acid, as well as by combustion with peroxide of copper. Both methods conspired to prove that hydrogen, which he had supposed to be one of its elements, is not really such. The constitution of the two acids is exhibited in the following Table:

	In indigotic acid.	In carbazotic acid.
Azote . . . . .	2 proportions.	4 proportions.
Carbon . . . . .	15 do.	10 do.
Oxygen . . . . .	10 do.	10 do.

The indigotic acid, therefore, contains 2 proportions less of azote, and 5 proportions more of carbon, than the carbazotic acid.

For the detail of the properties and composition of the class of salts called indigotates, I refer the reader to M. Buff's Memoir. (Ann. de Ch. et de Ph. Ju. 1829.)

*Kinic or Quinic Acid.*

MM. Henry, jun. and Plisson have extended their investigation of the kinic acid, and discovered new methods of preparing it. In appearance it resembles tartaric acid; it has a similar taste; and its specific gravity is 1.637. It is soluble in alcohol and in water, requiring of the latter, at 48° Fahr., about 2½ times its weight. It has the property of changing farina into sugar, and with alcohol gives an ether resembling that obtained by acting with tartaric acid on that fluid.

Analyzed with peroxide of copper, kinic acid gave,

Carbon .....	34.115
Hydrogen .....	5.560
Oxygen .....	60.325
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100.

The same authors have described the salts which kinic acid forms with bases, and recommend for trial the medicinal use of the kinates or quinate of cinchonia and quinia, as more analogous to the active principle existing in barks, than the sulphates of those alkaloids now so generally employed. (Ann. de Ch. et de Ph. July 1829.)

In speaking of the sulphate of quinia, I omitted to refer for the methods of detecting adulterations of it, now too much practised, to a paper by Mr. Richard Phillips in the Phil. Mag. and Ann. of Phil. Feb. 1828.

*New Earth discovered by Berzelius.*

Berzelius has announced, in a letter to M. Dulong, that he has discovered a new earth, in a mineral which is found very sparingly at Brévig, in Norway. Its properties bear a near resemblance to those of the supposed earth *thorina*, afterwards determined by Berzelius himself to be phosphate of yttria. He has therefore given to it (it appears to me not judiciously) the name of *thorina*, and to its metallic base the name of *thorium*.

The new earth is white, and is irreducible by charcoal and

by potassium. After having been calcined, it is attacked by no acid but the concentrated sulphuric, not even when previously acted upon by caustic alkalis. Its sulphate is very soluble in cold water, but almost insoluble in boiling water, insomuch that by the latter it may be obtained free from other salts. It is very soluble in carbonate of ammonia at common temperatures; heat precipitates a portion, which is redissolved on cooling. All its salts have a pure astringent taste, not unlike that of tan. Its chloride is decomposed by potassium with deflagration. A grey metallic powder results, which does not decompose water, but which, at a temperature above redness, burns with a splendor equal to that of phosphorus in oxygen gas. Nevertheless, thorium is feebly attacked by nitric and sulphuric acids. Muriatic acid, on the contrary, dissolves it with vivid effervescence. The oxide of thorium, or thorina, in 100 parts contains 11.8 oxygen. Its specific gravity is 9.4. (Ann. de Ch. et de Ph. Aug. 1829.)

*Spontaneous Diffusion of Gases through each other.*

This interesting subject, in which the first steps, made several years ago by Mr. Dalton, were afterwards followed up by Berthollet, has been recently pursued still farther by Mr. Graham, who has endeavoured to reduce the phenomena to fixed laws. (Quart. Jour. July—Sept. 1829.) He employed, in his experiments, a cylindrical glass receiver A, 9 inches in length and 0.9 inch internal diameter, divided into 150 equal parts, and provided with a stopper B, fitted into the mouth of the receiver by accurate grinding. The stopper was perforated longitudinally, (cavity 0.34 inch diameter,) and 1.8 long. Into its cavity was ground a short piece of stout tube C, having a bore 0.07 of an inch diameter, open at each end, and bent at a right angle; in some cases a wider tube than C was used, the diameter = 0.12 inch. The receiver was filled in succession with different gases in a state of purity. It was supported in a horizontal position upon a frame within a box, the open end of the tube C pointing downwards, when the gas was specifically lighter than atmospheric air, and upwards when heavier. Thus the gases were obliged, in escaping, to diffuse themselves in opposition to the solicitation of gravity.



The stoppers, in addition to being ground air-tight, were secured also by luting.

In the first set of experiments, after diffusion for ten hours, the receiver containing at the outset 150 measures of gas, there remained,

Gases.	Sp. gr. Air = 1.	Measures left in the receiver.	Escaped into the atmosphere.
Hydrogen . . . . .	0.0694	8.3	141.7
Carbureted hydr. . . . .	0.5555	56.	94.
Ammonia . . . . .	0.59027	61.	89.
Olefiant . . . . .	0.97220	77.5	72.5
Carbonic acid . . . . .	1.5277	79.5	71.5
Sulphurous acid . . . . .	2.2222	81.	69.
Chlorine . . . . .	2.5	91.	59.

After four hours, out of 152 measures,

Gases.	Left in the receiver.	Escaped.
Hydrogen . . . . .	28.1	123.9
Carbureted hydrogen . . . . .	86.	66.
Ammonia . . . . .	89.	63.
Olefiant . . . . .	99.	53.
Carbonic acid . . . . .	104.	48.
Sulphurous acid . . . . .	110.	42.
Chlorine . . . . .	116.	36.

If we attempt to deduce, from the foregoing Tables, the comparative diffusibilities of different gases, it will be necessary to keep in mind, that the rate at which the latter portions of gas leave the receiver is a diminishing one. In the case of olefiant gas, it was determined with precision, that the gas continues to leave a receiver by diffusion, according to the same diminishing rate, which holds in mechanical exhaustion by the air-pump. Hence the initial diffusions of the gases are even more varied than the numbers in the Table. As much hydrogen gas left a receiver in two hours, as of carbonic acid in ten hours; hence the former gas is five times more diffusible than the latter. Nor was the rate of diffusion that, which might have been expected from differences of sp. gr.; for carbureted hydrogen and ammoniacal gases left the receiver in greater proportions than olefiant gas, although the diffusion of the two former was more opposed by mechanical means. It is evident that the diffusiveness of the gases is inversely as some function of their density,—apparently the square root of their density.



The effect of the position of the receiver was shown by an experiment on hydrogen gas. Other circumstances being the same as in experiment Table 1, (where only 8.3 parts of hydrogen gas out of 150 were left after ten hours,) 22.1 parts were found remaining in the receiver, its position during that interval having been vertical, as in the figure.

The next object of Mr. Graham was to determine, whether, when an intimate mixture of two gases is left in the receiver, each gas leaves the receiver, independently of the other, in the proportion of its individual diffusiveness. For this purpose, the receiver was entirely filled with an intimate mixture of different gases in various known proportions to each other. For instance, equal volumes of hydrogen and olefiant gases (150 vols. in all), being left together ten hours, the following results were obtained :

	Found in the receiver.	Escaped.
Hydrogen gas . . . . .	3.5 . . . . .	71.5
Olefiant gas . . . . .	56.6 . . . . .	18.4
Air . . . . .	89.9	
	150.	150.

The most diffusive gas had, therefore, separated from the other, and left the receiver in the greatest proportion. On comparing these results with those of the foregoing Tables, it will be seen that the disparity between the diffusiveness of each of the gases, taken in a state of mixture, is actually greater than the disparity between the diffusiveness of the same gases compared separately. In the case of mixed gases, the law, as deduced from upwards of forty experiments on different mixtures, is,—that the more diffusive gas leaves the receiver in a *greater* proportion than in the case of the solitary diffusion of the same gas; and the less diffusive gas in any mixture, in a *less* proportion than in its solitary diffusion.

By availing ourselves of these tendencies in mixed gases to diffuse in different degrees, a sort of mechanical analysis of mixed gases may be carried on. Suppose, for example, we had a mixture in equal volumes of two gases, of the same densities as carbonic acid and carburetted hydrogen, not separable from each other by chemical means: allow this mixture to diffuse for a certain time, into a gaseous or vaporous atmosphere, of such a kind as

may afterwards be absorbed or condensed with facility. On condensing the latter atmosphere, there would remain a mixture consisting of one part of the light and one of the heavy gas. Continue these operations in a series, and the proportion of the light gas will progressively increase. If a specimen of the dense gas be required, a converse series of operations must be pursued.

Mr. Graham examined, also, the diffusion of gases into other atmospheres besides common air. A phial, containing 5.2 cubic inches, provided with a perforated cork, was filled with an intimate mixture of olefiant and hydrogen gases in equal proportions; and was connected, by a tube and another perforated cork, with a second bottle of the capacity of 37 cubic inches, containing carbonic acid gas. The phial had the highest station; and, to prevent contact with the external air, the apparatus was sunk in water below the joinings. After ten hours, the phial was found to contain, independently of carbonic acid, olefiant and hydrogen gases in the proportion of 12 to 3.1. In this case, the olefiant gas would undoubtedly have been obtained purer, had the original mixture been allowed to diffuse upwards.

The tendency to diffusion among gases being inversely as their densities, the lighter gases are more rapidly penetrated by any given vapour than the heavier ones. Hydrogen gas is expanded, for instance, by ether, four times more rapidly than atmospheric air. Consistently with the same principle, the heaviest vapours are by much the most slowly diffused; that of alcohol, for example, spreads more slowly through any gas than aqueous vapour. Expansion by heat increases the diffusive property; and in this way, Mr. Graham accounts for the increased facility with which gases, at a red heat, penetrate in both directions through porcelain tubes, and not from increased diameter of the pores of the porcelain.

It is to be hoped that Mr. Graham will fulfil his intention of returning to this curious investigation, and pursuing it still farther. He has judiciously refrained, in the present state of the inquiry, from drawing conclusions in favour either of the mechanical or chemical theory of the constitution of mixed gases; but every attentive reader will, I think, perceive that the tendency of the facts, so far as yet appears, is much in favour of the mechanical explanation.

### 3. *On the slow Oxygenation of Phosphorus.*

We are indebted to the same writer for the discovery of some curious facts, respecting the slow combustion of phosphorus; of which my limits permit me to give only a very brief outline. It had been known before, that phosphorus does not shine in oxygen gas under common pressures, and at temperatures below 69° Fahr. ; but that it exhibits the light, indicative of a slow combustion, when a pressure equivalent to two or three inches of mercury is taken off, or when the oxygen is diluted with a very small proportion of various other gases; but that it is not all gases, which qualify oxygen gas thus to act on phosphorus. Mr. Graham has gone farther, and has shown that there are certain vapours and gases, of which the presence, even in minute quantity, prevents the usual action of phosphorus on the oxygen of common air. Thus the slow combustion of phosphorus is entirely prevented, at the temperature of 66° Fahr., in mixtures of

	Vols. of air
1 vol. of olefiant gas with . . . . .	450
1 do. sulphuric ether with . . . . .	150
1 do. vapour of naphtha with . . . . .	1820
1 do. vapour of oil of turpentine with	4444

Phosphorus is not luminous in the dark, when surrounded by air slightly impregnated with any essential oil. It is extinguished by adding to air 4 per cent. of chlorine gas, or 20 per cent. of sulphureted hydrogen, and by the vapour of strong alcohol at about 80° Fahr. All the gaseous products of coal, too, protect phosphorus from oxygenation; but the vapours of camphor, sulphur, iodine, benzoic acid, carbonate of ammonia, and iodide of carbon, do not produce that effect at 67° Fabr.

It is remarkable that the influence of gases and vapours, in protecting phosphorus from slow combustion, continues at temperatures considerably elevated. But it is very curiously modified by a diminution of barometric pressure; for this allows the phosphorus to become luminous, in mixtures which had before prevented it from being so. The proportion, necessary to prevent combustion, depends entirely upon the density of the mixed gases. Thus, although less than one four-hundredth part of olefiant gas prevents the combustion of phosphorus, barom. 29 inches, yet phosphorus has been observed in a luminous state,

in air under the pressure of half an inch of mercury, containing so large a proportion as an equal volume of olefiant gas. (Quart. Journ. Oct. 1829.)

### *Oxides of Manganese.*

The analysis of the *manganite of Ihlefeld*, by Dr. Turner, who resolved it into a compound of 2 atoms of the deutoxide of that metal (together = 2 atoms base + 3 atoms of oxygen) with 1 atom of water, was confirmed by his subsequent examination of an ore of manganese found near Nuneaton, in Warwickshire, which appeared to be a precisely similar compound. Mr. Phillips, however, by whom Dr. Turner had been furnished with the latter specimen, having obtained different results, it became necessary that both those skilful analysts should re-examine the subject minutely. The event, while it has established the identity of the composition of Dr. Turner's specimen, with that of the Ihlefeld manganite, has shown that there is also another variety of the Warwickshire ore, the subject of Mr. Phillips's experiments, which very much resembles in external characters the true manganite, but yields, on analysis, proportions agreeing with 4 atoms of manganese, 7 atoms of oxygen, and 1 atom of water. To the new ore, which Dr. Turner, after a careful analysis of it, admits to be a distinct species, with the same proportions as stated by Mr. Phillips, the latter has given the name of *Varvicite*. Its specific gravity is 4.531, while that of manganite from Ihlefeld is 4.319, and of manganite from Warwickshire 4.336. The powder of varvicite is black, whereas that of manganite is brown; and the former ore may be scraped by a knife, somewhat more easily than the latter. At a white heat, true manganite yields no oxygen gas, but gives 10.1 per cent. of water; varvicite, at the same heat, loses 13.11 per cent., of which 5.725 are water, and 7.385 oxygen; whereas from the peroxide, as is well known, oxygen gas only is evolved under similar circumstances. The two former varieties are often found in the same specimen of the Warwickshire ore, and may be distinguished by a practised eye. By a white heat, all three arrive at the same stage of oxidation, *viz.*, at that of *red oxide*, described page 6. Varvicite is probably a compound of the previously known oxides of manganese, in the following proportions, as suggested by Mr. Phillips:

Manganese . . . . . $28 \times 4 = 112$ Oxygen . . . . . $8 \times 7 = 56$ Water . . . . . $9 \times 1 = 9$ <hr style="width: 20%; margin-left: auto; margin-right: auto;"/> Atomic weight . . 177	} or, {	Peroxide . . . . . $44 \times 2 = 88$ Deutoxide . . . . . $40 \times 2 = 80$ Water . . . . . $9 \times 1 = 9$ <hr style="width: 20%; margin-left: auto; margin-right: auto;"/> Atomic weight . . 177
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It is, however, obvious that varvicite may be considered as a compound of 1 atom of manganite (= 89) with 2 atoms of peroxide (= 88), together = 177. (See Ann. of Phil. March, April, and Oct. 1829.)

*Action of Caustic Potassa on Organic Substances.*

Vauquelin having converted the pectic acid into oxalate of potassa, by fusing it with that alkali in a crucible (see p. 707), M. Gay Lussac was induced to try the effect of treating ligneous matter in a similar manner. He found accordingly that cotton, heated over a spirit-lamp, with five times its weight of potassa prepared with alcohol, and moistened with a little water, was after some time softened, and that mutual action was evinced by a disengagement of hydrogen gas. The residuary mass, dissolved and supersaturated with nitric acid, gave with nitrate of lead abundance of oxalate of lead, which, when decomposed by sulphureted hydrogen, yielded fine crystals of oxalic acid.

Similar results were obtained by acting with potassa, in the same manner, on shavings of wood, on sugar, on starch, gum, and sugar of milk; and, which is still more remarkable, on tartaric acid, citric acid, and succinic and mucic acids; but benzoic acid withstood the action of the alkali. Acetate of potassa was transformed into the carbonate.

Among animal substances, silk, treated with potassa, gave oxalic acid with disengagement of hydrogen. Uric acid was acted upon with a formation of ammonia, and a white matter remained, from which nitric acid extricated hydro-cyanic acid and much carbonic acid; and the residuum contained oxalic acid. Gelatine underwent a similar change, but no oxalic acid was developed by acting with potassa on indigo.

Soda in a caustic state produced the same effects; but the alkaline carbonates have no power of causing the production of oxalic acid. It is probable that in some cases, beside the products already stated to accompany the oxalic acid, others may

be generated; and, till the nature of these has been determined, the theory of the changes cannot be fully developed.

M. Gay Lussac states, it should appear however not from his own experience, that, if crude tartar be dissolved in water, to which a due proportion of caustic potassa or soda has been added, and the solution be passed in a continual stream, by means of a pump, through a thick iron tube heated to between 390 and 480° Fahr., the tartar is converted into oxalate of potassa. The pressure in this case, since no gas is produced, may easily be regulated by a properly loaded valve, so as not to exceed 25 atmospheres. (Ann. de Ch. et de Ph. Aug. 1829.)

*New Principle in the Blood, distinctive of its Source.*

M. Baruel is said to have developed a principle in the blood of animals, by acting with a large excess of moderately strong and heated sulphuric acid upon the coagulum. An exceedingly volatile principle is extricated, accompanied with a strong odour of the cutaneous or pulmonary exhalation of the animal from which the blood has been drawn, an odour so characteristic, that it is easy to recognise the kind, and sometimes even the sex, of the animal to which it has belonged. To obtain these results, all that is necessary is, to put a few drops of blood, or of the serosity [serum?] of blood, into a glass; to add concentrated sulphuric acid to the amount of one-third or one-half; and to stir the whole together with a tube, when the peculiar odoriferous principle becomes evident.

The author of this discovery has applied it to discriminate, whether spots upon linen, apparently of blood, are caused by that fluid or not. The spotted part of the linen is to be cut out, put into a watch glass with a little water, and left for a short time, until well soaked. On adding concentrated sulphuric acid, and stirring with a glass tube, the peculiar odour is evolved. The process has been found effectual, when tried with linen which had been stained fifteen days; but if used with a view to judicial evidence, it is desirable to apply the test as soon as possible. (Quart. Journ. Oct. 1829.)

*Equivalents of Barium and its Compounds.*

I have noticed (vol. i. pp. 619, 629) the doubts that existed respecting the true equivalents of barium and its compounds, arising out of the contradictory statements of Drs. Thomson

and Berzelius, which required an appeal to further experimental evidence. The subject has been since investigated by Dr. Turner, of whose memoir, in the *Phil. Trans.* for 1829, a copy has reached me, at so late a period, as to allow me to state its substance in very general terms only. The principal cause of error, but not the only one, discovered by Dr. Turner, in the results of the first-mentioned philosopher, is, that on mixing solutions of chloride of barium and sulphate of potassa, in proportions supposed to be equivalent, the interchange of the elements of those compounds is not complete; a quantity of the former salt remains undecomposed in the liquid; and a portion of the alkaline sulphate adheres tenaciously to the precipitated sulphate of baryta. Avoiding this source of fallacy by the use of sulphuric acid, Dr. Turner obtained 112.19 parts of sulphate of baryta from the complete decomposition of 100 parts of pure chloride of barium; the proportions stated by Dr. Thomson being 111.32, and by Berzelius 112.18 parts. Again, 100 parts of pure anhydrous chloride of barium, decomposed by pure nitrate of silver, yielded 137.63 parts of chloride of silver, = 34.016 chlorine. From this fact, however, no decisive inference can be deduced respecting the atomic weight of barium, until the equivalent of chlorine is placed beyond all doubt. If the latter be taken at 36, the equivalent of barium will be 69.832; but, continuing the calculation on the same data, the equivalent of sulphuric acid will be 40.901, instead of 40; or, assuming with Berzelius 35.430 as the number for chlorine, barium will be represented by 68.726. These experiments, though insufficient to establish the true weight of barium, render it highly probable that it falls short of 70. The inquiry will be continued by Dr. Turner, with the view of deciding a point, not only important in itself, but affecting the atomic weights of many other bodies.





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C. Baldwin, Printer,  
New Bridge-street, London.

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