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By PROF. AUGUSTUS H. GILL OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

ENGINE ROOM CHEMISTRY

By HUBERT E. COLLINS

BOILERS SHAFT GOVERNORS ERECTING WORK PIPES AND PIPING KNOCKS AND KINKS PUMPS SHAFTING, PULLEYS AND BELTING

By F. E. MATTHEWS

REFRIGERATION. (In Preparation.)

HILL PUBLISHING COMPANY 505 PEARL STREET, NEW YORK 6 BOUVERIE STREET, LONDON, E.C.

Engine-Room Chemistry

A COMPEND FOR THE ENGINEER AND ENGINEMAN

BY

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THIRD IMPRESSION - THIRD THOUSAND





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PREFACE

THE object of this book, the substance of which appeared serially in *Power*,¹ is to enable the engineer or engineman to gain some familiarity with the properties and behavior of the substances, as fuel, water and oil, in which he is vitally interested, and some suggestions and assistance in connection with their use.

A knowledge of chemistry and physics, such as may be obtained from the "Science Primers"² or a high school course, is very desirable, one might almost say indispensable. Chapter I will serve as a review of certain topics from these branches of science.

A careful study of the applications of fuel, water, and lubricants cannot but result in increased economy in their use, and if this little book renders this study easy the writer's purpose will have been accomplished.

The apparatus can be obtained from the leading dealers in New York City.

Boston, Mass., July, 1907.

AUGUSTUS H. GILL.

¹ Power, May, 1905, to July, 1906.

² "Chemistry," H. E. Roscoe; "Physics," Balfour Stewart. American Book Company, New York.



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INTRODUCTORY — CHEMICAL AND PHYSICAL CHANGES—CHEMICAL SYMBOLS EXPLAINED

1

THE two terms "chemistry" and "physics" can perhaps be best defined by saying that chemistry has to do with chemical changes, or is the science of chemical changes, whereas physics deals with physical changes. A chemical change is one in which the nature of the substance is altered. For example, when iron is changed by exposure to iron rust it is changed chemically; we can no longer recognize any semblance of metallic iron in the reddish-brown powder before us, nor can we by mechanical means get the bright metallic iron back again; chemical means must be employed. On the other hand, a piece of iron may be chipped or filed reduced to powder; but it still retains its metallic appearance or luster, and may by melting and working be brought back to its original form. In other words, through all these processes it always remains iron; hence it is changed physically, not chemically. Again, we may mix iron filings and finely powdered sulphur, obtaining a powder resembling neither: it is only a mechanical mixture. This can be shown by separating the iron by a magnet, or the sulphur by solu-

I

tion ¹ in carbon bisulphide: if we heat some of the mixture it begins to glow, the glow extends throughout the mass, and, after cooling, on examination we find a fused substance which is neither magnetic nor soluble in carbon bisulphide, and from which the iron and sulphur can be separated only by chemical processes — a chemical compound, sulphide of iron.

Other examples of chemical changes will no doubt present themselves on reflection, e.g., the "souring" of milk and cider; the fermentation of beer, in which sugar or molasses is changed to alcohol and carbonic acid; the burning of fuel, etc. Physical changes are seen in the drilling and bending of metals, the melting of lead and solder, the breaking of stone, etc. Chemistry is sometimes spoken of as the science that deals with atoms, while physics deals with molecules: this is another way of saying that these are the units with which these two sciences largely deal. By "molecule" we understand the smallest particle of a substance that can exist by itself and be that substance; while an atom is the smallest particle of a substance that can exist in combination with other atoms, either like or unlike. Molecules are made up of atoms which are either similar or dissimilar; and all substances are

¹ By the term "solution" is meant the division of the particles of a solid among the particles of a liquid, so that the former become invisible and cannot be separated by filtering, that is, straining through filter paper. By evaporation, or boiling off the liquid, the solid is recovered again unchanged. This is known as physical solution. When, in making soldering fluid, zinc is "dissolved" or "cut" with muriatic acid, that is said to be a chemical solution, because on its evaporation a different substance from zinc — a white solid, zinc chloride — is obtained. When oil is mixed with water an emulsion like milk is obtained, which in time separates. So when clay is mingled with water, a suspension rather than solution is produced, because after a time the clay settles out.

made up of molecules. If the atoms that go to make up a molecule are of the same kind, the substance composed of such molecules is said to be an elementary substance or an *element*. Such are: the metals, as iron and copper; the non-metals, as sulphur and carbon (seen in charcoal); the gases, as oxygen and nitrogen (existing mixed in the air); and some seventy others. On the other hand, if the atoms making up a molecule are unlike, the substance is said to be a compound. This is illustrated in sulphide of iron, carbonic acid, and practically all the substances with which we come in contact.

Besides writing "sulphide of iron," "carbon," "sulphur," etc., chemists are in the habit of designating all substances elementary and compound, as far as possible, by *symbols*. These symbols mean very much more than the "ferr. sulph.," "pot. nitr.," or other abbreviations of the apothecary: they show, by a small figure written after the element and below the line, the number of atoms of each element in the substance, and, as each of these atoms has a definite weight, the percentage of each element present. Moreover, in the case of what are called "displayed" or "graphic symbols," they show the way and manner in which the various atoms are combined with each other. or, in other words, the constitution of the substance. In the case of gases, the symbol shows furthermore their volumetric composition. For example, the sulphide of iron mentioned above has the formula or symbol FeS; but as there are other combinations of iron and sulphur to which the term "sulphide of iron" is equally appli-

cable, as FeS, and Fe₂S₃, the symbol FeS states just which this one is, namely, ferrous sulphide. It indicates furthermore that it is composed of one atom of iron and one atom of sulphur, or 56 parts by weight of iron and 32 parts by weight of sulphur, or $\frac{56}{32+56} = \frac{56}{88}$ or 63.6 per cent. iron, and $\frac{32}{88}$ or 36.3 per cent. of sulphur. In the case of sulphurous acid, SO₂, the formula shows it to be made up of one atom of sulphur combined with two atoms of oxygen, whence it receives the exact name of sulphur dioxide (di = Greek word for "two") or 32 parts of sulphur and 32 parts of oxygen, or $\frac{3}{6}\frac{2}{4}$ or 50 per cent. of sulphur and $\frac{3}{6}\frac{2}{4}$ or 50 per cent. oxygen. Besides this, the symbol shows it to be composed of one double volume of sulphur vapor with two double volumes of oxygen gas, making two double volumes of sulphur dioxide.



So it is with every definite chemical compound. These weights of the elements, with which we have been dealing, in which they combine, are spoken of as *atomic weights*. The story of their determination would take us beyond the limits of the present work. Suffice it to say that they are fixed by extremely careful analyses of absolutely pure compounds containing the element the atomic weight of which is to be determined.

INTRODUCTORY

Table I gives the list of the elements with whose compounds we are likely to meet, together with their atomic weights.

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LIST OF COMMON ELEMENTS AND THEIR ATOMIC WEIGHTS

		1		1	1
	Element	Symbol	Atomic Weight	Source '	Familiar Compound
Alu	minum	Al	27.1	Clay	Alum
Bai	rium	Ba	137.4	Barytes	Barium chloride
Cal	cium	Ca	40.1	Lime	Gypsum, chalk, marble
Cai	bon	C	12.0	Charcoal	Graphite, diamond
Chl	orine	Cl	35.5	Salt	Chlorides, salt
Cop	oper	Cu	63.6	Native	Copper sulphate, "blue-
(I	latin, cuprum)			copper	stone "
Hye	drogen	H	0. I	Water	Hydrates
Iron	n	Fe	55.9	Iron ore	Iron rust
(I	at. ferrum)				
Lea	ıd	Pb	206.9	Galena	Lead acetate, sugar of
(L	at. plumbum)				lead
Ma	gnesium	Mg	24.4	Chloride	Magnesite, Epsom salts
Me	rcury	Hg	200.0	Sulphide	Calomel, corrosive sub-
(I	Iydrargyrum)				limate
Nit	rogen	Ν	14.0	Air	
Oxy	ygen	0	16.0	Air	
Pho	sphorus	Р	31.0	Bones	Phosphates
Pot	assium	K	39.1	Potash	Niter
(L	at. kalium)				
Sod	ium	Na	23.0	Salt	Soda ash, salt
(L	at. natrium)				
Sulj	phur	S	32.0	Native	Brimstone
				sulphur	
Zin	c	Zn	65.4		Zinc white

Table II shows some of the more common compounds containing the above elements.

Chemical Name Symbol Popular Name $Al_2O_3 + SiO_2 + H_2O$ Aluminum silicate Clay $K_{2}Al_{2}(SO_{4})_{4} + 24H_{2}O$ Aluminum and potassium sulphate Potash alum BaSO₄ Barium sulphate Barvtes $CaSO_4 + 2H_2O$ Calcium sulphate hydrated Gypsum Plaster of Paris CaSO4 Calcium sulphate CaO Calcium oxide Lime Calcium hydrate CaO₂H₂ Air-slaked lime Calcium carbonate Chalk, limestone, mar-CaCO. ble CaH₂(CO₃)₂ Calcium bicarbonate Bicarbonate of lime CaCl₂ Calcium chloride Same Carbon monoxide CO "After damp," carbonic oxide "Whitedamp," "choke CO2 Carbon dioxide damp," carbonic acid HCl Hydrochloric acid Muriatic acid $\operatorname{CaCl}_2^+ = \operatorname{CaOCl}_2$ (Calcium chloride Chloride of lime CaCl₂O₂ Calcium hypochlorite Bleaching powder H,O Hydric oxide Water Fe2O2 Ferric oxide Iron rust Ferroso-ferric oxide Fe₃O₄ Forge scale FeCO₃ Ferrous carbonate Carbonate of iron FeH₂(CO₂)₂ Ferrous bicarbonate Bicarbonate of iron PbCO, White lead Lead carbonate PbO Lead oxide Litharge MgO Magnesium oxide Calcined magnesia Magnesium carbonate Magnesite, magnesia MgCO.

TABLE II

INTRODUCTORY

TABLE II - Continued

Symbol	Chemical Name	Popular Name		
MgH ₂ (CO ₃) ₂	Magnesium bicarbo- nate	Bicarbonate of mag- nesia		
MgCl ₂	Magnesium chloride	Same		
HNO,	Nitric acid	Aqua fortis		
NH,	Ammonia	Ammonia		
Ca ₂ P ₂ O ₈	Calcium phosphate	Bones		
KNO,	Potassium nitrate	Niter		
K ₂ CO ₃	Potassium carbonate	Potash or pearl ash		
KOH	Potassium hydrate	Potash lye, caustic potash		
NaCl	Sodium chloride	Salt		
$Na_2CO_3 + H_2O$	Sodium carbonate hy- drated	Washing soda, soda crystals		
Na ₂ CO ₃	Sodium carbonate	Soda ash		
NaHCO3	Sodium bicarbonate	Baking soda		
NaOH	Sodium hydrate	Soda lye, caustic soda		
SO ₂	Sulphur dioxide	Sulphur fumes, sul- phurous acid		
H ₂ SO ₄	Sulphuric acid	Oil of vitriol		

A point to be observed in this connection is that the elements combine in certain definite proportions. Reverting to our experiment of heating sulphur and iron together, if we were to mix 56 ounces or pounds of sulphur with 56 ounces or pounds of iron and heat them, we should find, after the reaction was finished, that there was a residue of uncombined sulphur amounting to 24 ounces or pounds as the case might be. So that the proper mixture would be 56 parts of iron to 32 parts of sulphur, any excess of either being left uncombined.

Chemical Reactions or Equations. — In all the text-books of chemistry, one finds expressions like this, Fe + S = FeS, which is the chemist's way of saying that when iron (Fe) and sulphur (S) unite under certain circumstances, ferrous sulphide (FeS) results. From what has been stated in the preceding paragraph, more than this is, however, here expressed; namely, that when 56 parts by weight, be they ounces, pounds, or grams of iron, and 32 parts by weight of sulphur combine, 88 parts by weight of ferrous sulphide are produced.

Every simple chemical action can be thus expressed. It is a question of determining what factors enter into the action and what products are formed, then totaling them on each side, and putting the sign of equality between the sum of the factors and the sum of the products. For example, when lime (quicklime) absorbs water from the air and makes "air-slaked lime"

```
\begin{array}{rll} CaO & + & H_2O & = & CaO_2H_2 \\ quicklime & water & air-slaked lime \\ 4\circ + & 16 + & (2 + 16) = 4\circ + & (2 \times 16) + & (2 \times 1) \\ & & 56 + & 18 = 74 \end{array}
```

These equations tell us further, how much of one substance (quicklime) must be used to absorb the other (water), and how much air-slaked lime-will be produced. Reading this equation we see that, to absorb 18 pounds of water, 56 pounds of quicklime must be employed, and that 74 pounds of slaked lime would be produced. If it were a question of absorbing 100 pounds of water, we could make the proportion, weight of water : weight of quicklime needed :: molecular weight of water : molecular weight of quicklime, or 100 : x :: 18 : 56. Whence 18x = 5600. x = 311 + 1b.

In looking over Table II we see some compounds designated as acids, *e.g.*, HCl, hydrochloric acid; H₂SO₄, sulphuric acid; HNO₃, nitric acid; and the question may very properly arise, what an acid is. Chem-ically speaking an *acid* is a compound of hydrogen, a non-metallic element and usually oxygen: this hydrogen is replaceable by a metal, forming a salt. Acids generally have a sour taste and turn blue litmus paper red. When "soldering acid" is made by "dissolving" zinc in muriatic acid, bubbles of gas are given off, which are the hydrogen that is replaced by the zinc; and if we were to evaporate the liquid resulting, we should get a white solid, "muriate of zinc" or zinc chloride. Exactly opposite in character to the acids are the bases, which they resemble in containing hydrogen and oxygen; but in place of the non-metallic or negative element they have a metallic or positive element. Such in the table are: CaO₂H₂, air-slaked lime or calcium hydrate; KOH, caustic potash or potassium hydrate; NaOH, caustic soda or sodium hydrate. They have a biting taste, a "soapy feel" - actually dissolving the skin - and turn red litmus blue. They unite with acids, forming salts: if we neutralize caustic soda with muriatic acid and evaporate the solution obtained, we get common salt. We can conversely obtain the base from common salt by the electric current, as is done on an enormous scale for paper-makers and others.

Again, on inspecting Table II we notice

$CaCl_2$	NaCl				
CaO_2H_2	NaOH	KOH	CaCO ₃	Na_2CO_3	K_2CO_3

Why this diversity of numbers? It is due to the fact that the elements calcium (Ca), sodium (Na), and potassium (K) have a different replacing power as regards hydrogen. That is, while sodium (Na) replaces one atom of hydrogen (H) in HCl, calcium (Ca) replaces two atoms in two molecules of HCl, 2HCl or H₂Cl₂. Sodium is said to be univalent, that is, worth one (uni = one, valeo = to be worth), or will replace or combine with one atom of hydrogen or chlorine; similarly, calcium is bivalent (bi = two), iron is trivalent (tri =three), and carbon is quadrivalent (quadri = four). Other univalent elements in the table are chlorine and hydrogen: bivalent elements are barium, calcium, copper, lead, magnesium, mercury, oxygen, and zinc; trivalent elements are aluminum, iron, nitrogen, and phosphorus; quadrivalent elements are carbon and silicon

CaCO ₃	Na_2CO_3	K_2CO_3
$CaCl_2$	NaCl	

In this case, the diversity of numbers is due to the fact that in addition to elements like sodium and calcium, which are univalent and bivalent, that is, replace respectively one atom and two atoms of hydrogen, we have acids corresponding, which have one atom

10

and two atoms of hydrogen which can be replaced: such acids are said to be monobasic (mono = one) and dibasic (di = two). When a bivalent element, as calcium (Ca), combines with a dibasic acid as carbonic H₂CO₃, both atoms of hydrogen are replaced and we get a salt CaCO₃, so CaSO₄, BaSO₄, MgCO₃, etc. When a univalent element Na' so combines, two atoms of the element Na₂" are required to form a neutral salt Na₂CO₃, so K₂CO₃; sometimes only one hydrogen atom replaced and we get an acid salt NaHCO₃. When a univalent element, as sodium (Na), combines with a monobasic acid, as hydrochloric (HCl), one atom of hydrogen is replaced and we get a salt, NaCl, so KCl, KNO₃, etc.; when a bivalent element (Ca") combines with a monobasic acid two molecules of acid (H₂Cl₂) are required to form a salt, CaCl₂, so MgCl₂.

It will be observed that in the foregoing, all references have been made to minerals or metals, all illustrations have been taken from "inorganic chemistry" as it is termed. There is another branch of the science, which, from its intimate connection with organized life, is designated "organic chemistry." It was formerly supposed that for the production of its compounds, life of some kind was necessary, and that they could not be made in the laboratory from inorganic

materials. In 1828 Woehler made urea, CO а

substance known only to occur in urine, by heating ammonium cyanate (NH₄CNO), an inorganic compound. He was the first to erase the hard and fast line separating these two subdivisions; it is better termed the chemistry of the carbon compounds. Carbon not only combines with other elements as do other elements, but it possesses the property of combining with *itself* to a very marked degree. Its combination with hydrogen, CH_4 , is known as marsh gas or the "fire damp" of mines; another, $CH_3 - CH_2 - CH_2 - CH_2 - CH_2$ $CH_3 = C_6H_{14}$, a liquid, is the chief constituent of gasolene, and still another, $CH_3 - CH_2$, $- \text{etc.} - CH_3 =$ $C_{24}H_{50}$, a solid, is contained in paraffin wax. The compounds between C_6H_{14} and $C_{24}H_{50}$ occur in the kerosenes and the mineral lubricating oils.

Organic Chemistry is the chemistry of the necessities of life — food, clothing, and raiment — of digestion, assimilation, growth, and decay, and of the accessories of life, as the alcoholic beverages, the brilliant aniline dyes and the perfumes.

Chemical Analysis is divided into two parts:

(1) *Qualitative Analysis*, in which the components of a substance are determined, and which answers the question "Of what is a substance composed?" and

(2) *Quantitative Analysis*, in which the percentages of these components are fixed.

While it is possible to determine with reasonable accuracy the elements and their percentages which make up certain compounds, as a boiler scale or an alloy, or "of something of a mineral or metallic substance" or inorganic bodies, such is not always the case with compounds containing carbon or organic substances. For example, it is practically impossible to ascertain to what extent an asphalt paint is adulterated with gas, wood, or petroleum tar.

This brings me to speak of the two subdivisions of both qualitative and quantitative analysis — ultimate and proximate. An ultimate analysis states simply the percentages of the various elements present, while a proximate analysis states the substances of which it is composed. For example, the ultimate analysis of a white powder shows it to contain carbon, hydrogen, and oxygen in certain percentages. This tells little of practical value about it. By suitable means, however, we ascertain that it is made up of 50 per cent. starch and 50 per cent. sugar, and no one would have the slightest trouble in duplicating it.

The principle in the qualitative analysis of substances consists in the production either of a definite precipitate or "sediment" containing the element sought, or of a colored compound, or both, which can only be formed when the element in question is present.

In quantitative analysis a substance is estimated in two ways: (1) by weighing it, gravimetric analysis; (2) by measuring it, volumetric analysis, or rather by measuring an acid or alkali necessary to neutralize or dissolve it.

(1) In gravimetric analysis a weighed amount of the substance is precipitated under definite conditions, forming a compound of definite composition which is not dissolved by the liquids in which it is formed. This compound is filtered off, "strained" through specially prepared paper which collects it completely, the paper burned and compound heated, often to redness,

giving a compound of definite composition free from water. This is weighed, and from its known composition, the amount of the element sought, calculated, whence its percentage in the substance under examination can be found. For example, to estimate the amount of lime in a boiler scale, the scale is dissolved in pure muriatic acid, the solutions boiled down completely or, as the chemist says, evaporated to dryness, heated to render silica (sandy matters) insoluble, redissolved in water with the addition of acid by heating, and neutralized with ammonia: this throws down any iron or alumina (clayey matters) that might be present, leaving in solution nothing but lime, magnesia, soda, and potash. Under these conditions, if ammonium oxalate be added, oxalate of lime (calcium oxalate) and nothing else is thrown down, and, as it is not dissolved by the liquid present, the lime is precipitated completely. The precipitate of calcium oxalate is collected on a filter, the filter burned in a weighed crucible, the precipitate heated to a white heat, whereby it is changed to quicklime and weighed. The gain in weight after deducting the filter ash represents the amount of lime (calcium oxide) in the scale.

(2) Volumetric Analysis. An example of the application of volumetric analysis is found in the determination of the alkaline strength of caustic soda. A weighed amount is dissolved in water in a flask, litmus solution added, and standard hydrochloric acid run in from a burette or measuring-tube until the solution turns faintly red. As every cubic centimeter of the acid corresponds to a definite amount of caustic soda or will neutralize it, from the amount of acid used, the amount of caustic present can be calculated. This kind of analysis is rapid and accurate, and it has a very wide application.

Π

APPARATUS AND CHEMICALS — CHEMICAL TESTS

Some one has said that it is not sufficient to know the principles of a science: one must also be able to manipulate or handle the tools. The tools which the chemist uses are very varied and comprehensive, including not only those usually employed by all mechanics, but also those peculiarly his own — the delicate balance and the powerful crusher, strong acids and alkalies, and the means of production of intense heat as the gas-burner and even the electric furnace.



Mortar

Sampling and Grinding Apparatus. — The ordinary *coffee-mill* set fine will serve to grind coal finely enough for the moisture determination. For calorimetric or chemical tests it should be ground three times in the mill and finished by grinding in a 5-in. *iron mortar* (Fig. 1), and passed through a 100-mesh sieve. Any

particles remaining on the sieve should not be thrown away, but should be returned to the mortar and reground.

A 4-in. *palette knife* is very useful for handling and weighing out these powdered samples.

Weighing Apparatus. — For the necessities of this book the weighing can be done on *horn pan* or *photographic scales* with $7\frac{1}{2}$ -in. beam (Fig. 2), with metric weights to 100 grams. They consist of a beam, from



FIG. 2. - Horn Pan Scales

each end of which a horn pan is suspended by means of silk threads. The beam is provided with a pointer; and the scales are sensitive to 0.01 gram, that is, they will show differences of 0.01 gram. The weights from this up to 100 grams are contained in a wooden block. To protect the scales from drafts they may be hung inside a box.

The operation of weighing is conducted by laying the substance to be weighed on the left-hand pan and placing the weights on the other — handling them with pincers to prevent them from being corroded. To save time, the weights are always placed on the pan in regular order, beginning with the heaviest that it is judged that the object will weigh; and the operation is continued until the scales just balance, or, better, swing to the same distance each side of the stirrup which supports them. The weight of the substance is read off from the block, set down in a note-book provided for this purpose — not on loose paper — and is checked by putting each weight into its proper place.

For heavier objects, scales of the type of a grocer's small tea scales, with porcelain plate may be recommended.

Measuring Apparatus. — Liquids are measured by graduates for coarse work, and by graduated flasks,



burettes, and pipettes for accurate work. *Graduates* (Fig. 3) are tall graduated tubes with a lip for pouring and a foot upon which they stand. Those holding 50 cubic centimeters (cc.) are most convenient: they are to be had in various sizes to a liter (1000 cc.).

Graduated flasks (Fig. 4) have a line upon their necks which shows the hight to which they must be filled to contain a certain quantity, as a fluid ounce, or more usually cubic centimeters. They should be filled so that the lowest part of the curve which the liquid assumes—the meniscus—just touches the line.



FIG. 4.— Graduated Flask

A 50-cc. flask will be required to measure the water for the hardness test.

A burette (Fig. 5) is a tube graduated like an engineer's scale into whole divisions and tenths, usually into cubic centimeters and tenths, and provided with an outlet at the bottom closed by a glass stopcock, or ball valve and jet. By pinching the rubber tube enclosing the ball valve, a channel is made for the liquid to run out. The burette is held by a clamp in a vertical position and the liquid read in the same way as in the case of the graduated flask. The apparatus is filled with the standard solution of soap by pouring it in through a funnel.



Apparatus for the Production and Application of Heat. — *Lamps and Burners*. Where available, gas is the most satisfactory source of heat and is burned in the *Bunsen*



FIG. 6. — Bunsen Burner

burner (Fig. 6). This consists of a straight tube provided with air inlets near the bottom. The gas, entering by a jet at the center of the tube, sucks the air necessary for

its combustion through these inlets and burns with a colorless flame, giving a temperature of about 2300 deg. F. Where gas is not obtainable, some form of vaporizing gasolene burner, as seen in the plumber's furnace or lamp for soldering, can be used to good advantage. These employ the same principle as the gas-burner: the gasolene is forced by air-pressure through a hot coil of pipe which changes it to vapor, and this mixes with air and burns like a fixed gas. Instead of these, the common alcohol lamp may be used for most purposes.



Blowpipes. These (Fig. 7) consist of a tube bent as in the figure, used largely by mineralogists to direct a lamp or candle flame upon a substance to be heated. Charcoal or strips of plaster of Paris are used as supports for the substance. When the blowpipe tip is put into the flame and the mouthpiece blown into, a long, hot, pointed flame is produced, hottest just beyond the tip of the blue cone. This is known as the oxidizing flame, because it oxidizes, tarnishes, or burns substances heated in it. The oxides or "rusts" of some of the metals coat the charcoal with characteristic colors. Similarly, when the blowpipe tip is held just outside the smoky flame, a reducing flame is produced, which directed upon the substance takes oxygen away from it or "reduces" the rusts or oxides of the metals to the metals themselves. If the substance contains sulphur, as a sulphate, by heating it with charcoal and soda in this flame, a sulphide is produced, a lump of which placed upon a silver coin and moistened, gives a characteristic black stain of silver sulphide. This test can be used to test for sulphates in boiler scales and for sulphur in coal.



FIG. 8. - Crucible

Crucibles. These (Fig. 8) are narrow, deep vessels of fire-clay. Those made in Battersea, England, size C, are the ones used in the Berthier test. They are also made in the finest Berlin and Meissen porcelain: size No. 7 is the best adapted for our work.

Closed Tubes or Matrasses. These are of hard, that
is difficultly fusible, glass about $\frac{1}{4}$ -inch in diameter and 3 inches long, and are used for observing the behavior of substances when exposed to the heat of the Bunsen burner in the Closed Tube Test as it is called.

Drying Ovens. These may be made in various ways and of various materials: for permanent fixtures those of copper or metal-lined wood are to be recommended. Copper ovens are heated by gas or steam, and this latter agent is employed with the latter type of oven. For our purposes a square tin or iron box heated by a gas-burner or kerosene stove and provided with a thermometer will serve admirably.



FIG. 9. - Porcelain Dish

Containing and Handling Apparatus. — Funnels and Filters. Chemists' funnels are exactly like the household article in "tin" — tinned iron — except that they are made of glass and from $2\frac{1}{2}-3$ in. in diameter. They are used largely as supports for filters. Filters are disks of unsized paper (filter paper) three or four inches in diameter. They can be most simply folded as to make a half-circle, and this folded to make a quarter-circle, opened and placed in the funnel. Other methods of folding are illustrated in the books on analysis. It is well to moisten them with hot water before filtering through them.

Porcelain Dishes. These (Fig. 9), like the crucibles, are of the finest porcelain and are used as vessels in

which to dissolve substances and boil them down. The Berlin dishes glazed within and without are the best; the 3-in. dish will be found large enough for all purposes mentioned here.

Test-tubes. Test-tubes are cylinders of thin glass (Fig. 10), sealed round at the bottom, about six inches long and $\frac{5}{8}$ in. in diameter. As their name



denotes, they are used for testing purposes. When heated they are held in wooden tongs and, like firearms, should never be pointed toward oneself or any one else. When not in use they are supported in a rack or a block of wood having 12 holes and six pegs.

Beakers. When considerable quantities of liquid are to be employed, particularly when heated, wider

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vessels of thin glass called beakers (Fig. 11) are used, the common sizes being from an ounce to a pint. Both



beakers and test-tubes may be cleaned with a test-tube brush.

A wash-bottle (Fig, 12) is a very convenient means of



keeping at hand a supply of distilled water from which to pour small quantities when required. By blowing into the mouthpiece a stream of water is expelled from the jet, which is used to wash precipitates, etc. The distilled water can be obtained by catching the condensed water from "returns" and will be found pure enough for all our purposes. Ordinary tap water is too impure for refined analytical work.

Miscellaneous Apparatus. — Iron stands and rings (Fig. 13) or tripods are used to support vessels over a lamp for heating. The apparatus usually rests on



FIG. 13. - Iron Stand

wire gauze upon the ring. This gauze seems to protect the beaker from the intense heat of the flame. When heating a vessel containing a liquid, drops of water from the lamp flame are usually deposited upon it: as these are apt to run together and down upon the hotter part of the vessel and crack it, they should be wiped off from time to time. For supporting crucibles, iron-wire triangles covered with clay piping pipe-stem triangles — may be used.

Thermometers. What are known as chemical thermometers, those with the divisions of the scale etched on the stem, with a milk-glass back, are to be preferred. They should be divided into two degrees and for ordinary purposes should register to 680 deg. F.: for testing cylinder oils they may read to 800 deg. For higher temperatures to 1000 deg. F. the "high-temperature thermometers," which are filled with carbonic acid or nitrogen under a pressure of about 100 lb., may be used. These are usually encased in a bronze or iron tube. For taking chimney temperatures a thermometer should never be inserted naked into the flue, as a blast of gas at a high temperature may strike and burst it: temperatures as high as 1150 deg. F. have been observed for a few moments in chimneys. A bath of heavy cylinder, linseed or cottonseed oil contained in a plugged 1/2-in. pipe should be inserted into the flue or duct and the thermometer placed in this. Thermometers should be tested from time to time, and as nearly as possible under the conditions under which they are used, *i.e.*, with the same amount of stem projecting. To this end they should be placed in a bath of melting ice which practically shows a temperature of 32 deg. F.: water can be boiled in a plugged piece of 11-in. pipe and the thermometer suspended in the steam — not dipped into the water — when 212 deg. F. should be indicated. If the water be replaced by naphthalene and the latter be heated to boiling, a temperature of 426 deg. F. is obtained in the vapor.

When it is not practicable to use thermometers, as with locomotives, the temperature may be obtained by taking the melting-points of pieces of certain metals, or of some salts contained in small cast-iron boxes (Fig. 14). The metals and salts available with their melting-points will be found in Table VIII of the Appendix. In the case of salts they should be dried for two hours in the oven at 220 deg. F. For the measurement of still higher temperatures electrical and optical pyrometers are used.



FIG. 14. — Meltingpoint Boxes

Calorimeters. Thermometers and pyrometers show simply the intensity of the heat, just as a water-gage shows the pressure on a service pipe. They show the highest temperature produced by the combustion of coal or gas without giving any idea of the *quantity* of heat produced. For this measurement calorimeters are employed, just as a water-meter is used to show the amount of water used.

To determine the heating value of a fuel (for which

specific directions will be given in Chapter III) it is burned, in one method, in a closed bomb, which is submerged in water in a copper vessel. The temperature of the water is read both before the coal is ignited and afterward, and the rise of temperature found. Knowing, besides this, the weight of water and its specific heat, the total amount of, heat generated by the fuel can be determined; and this, divided by the weight of coal burned, gives the number of heat units or British thermal units (B.t.u.).

Specific Heat. - This term has been used in the preceding paragraph. For it, however, "calorific capacity" could be substituted. By it we mean the power which a substance has of absorbing heat. If we place an ounce of mercury and an ounce of water at equal distances from the same source of heat and allow them to remain for the same length of time, we shall find that the mercury becomes much the hotter about thirty times as hot in fact - it has a low specific heat; that is, it takes only about one-thirtieth as much heat to raise the temperature a given amount as it would to raise its temperature of an equal weight of water an equal number of degrees. Water has the greatest specific heat of any substance,1 and is taken as the standard, or 1.000. The specific heats of all other substances are therefore expressed in fractions.

That quantity of heat necessary to raise the temperature of one pound of water one degree Fahrenheit is called a British thermal unit, and is used as the standard unit in America and in England. If we substitute for this one kilo of water and one degree Centigrade

¹ Excepting hydrogen.

we have the French or scientific unit: it is equal to 3.96 B.t.u. On the other hand, if a pound of coal yield 14,500 B.t.u., the number of calories that it would yield per kilo is found by dividing the number of B.t.u. by 1.8, the equivalent of the Centigrade degree in Fahrenheit degrees; the English equivalent of the kilo, 2.2 pounds, cancels out, being in both numerator and denominator.

Thermometer Scales. —The scale proposed by Fahrenheit in 1714 is still used in England and in America: his zero was the lowest temperature then obtainable — by ice and salt. Ice melted at 32 of his degrees above this, and water boiled at 180 degrees higher. Celsius' scale started with the melting-point of ice as o, and the boiling-point of water as 100, and divided this distance into one hundred equal parts or degrees, whence it is called the Centigrade (100-degree scale). Thus 180 deg. F. = 100 deg. C.; or one deg. F. = $\frac{9}{5}$ deg. C.; or 1 deg. C. = $\frac{9}{5}$ deg. F. Table IX in the Appendix shows the relation between the two scales.

Reagents. — Besides these mechanical aids or tools, the chemist has to employ chemical aids, or "reagents," as they are called, because they bring about certain characteristic reactions or tests. Those for our immediate purposes are not numerous, but in connection with a book on qualitative analysis, may be increased so that a considerable range of work may be done.

Reagents should be kept in well-stoppered and correctly labeled bottles of heavy resistant glass, specially made to withstand the wear and tear of use, as well as the action of the chemicals themselves. A size hold-

ing a half-pint (250 cc.) is most convenient. In using, them, care should be taken never to lay the stoppers upon the desk or table, as some dirt may adhere to their wet surface and thereby get into and contaminate the reagent. When they have been unused for a considerable time the crust forming on the lips of the bottle should be carefully washed off. In case the stoppers stick they can usually be started by gentle tapping with a hammer. Care should be exercised at all times to keep them pure. As many of them are poisons, they should be kept under lock and key, best in a wooden cupboard with a light in front of it, provided with bronze hinges, hasp and padlock. Iron trimmings and locks are more susceptible to corrosion. Care should be also taken to keep them, and in general to perform experiments in which they are used, in a room away from anything that would be corroded, rusted, or otherwise injured by their fumes; for some of them are acid.

The reagents required for our work are comprised in the following:

Acids. Nitric (HNO₃), hydrochloric (HCl), and sulphuric (H₂SO₄) acid, all strong and chemically pure (C.P.), should be handled with great care. In case they get upon the skin or clothes, they should be washed off at once with water and afterward with a little dilute ammonia. They are used strong, and also diluted 1 part to 4 parts of water, *pouring the acid into the water*. If the operation be reversed, particularly with sulphuric acid, explosions may occur which will scatter it about.

Ammonium Hydrate, "Ammonia" (NH₄OH). Di-

lute the ordinary strong ammonia with an equal volume of water or use "Household Ammonia." Used to test for aluminum (Al).

Ammonium Chloride (NH₄Cl). I part to 10 of water. Place 2.5 grams of the C.P. salt in a reagent bottle, add 250 cc. distilled water and shake. The exact amount of water makes no difference; the bottle could be filled to within half an inch of the top.

Ammonium Oxalate $(NH_4)_2C_2O_4$. I part to 10 of water, as above under ammonium chloride. Used to test for lime (Ca).

Barium Chloride (BaCl₂). I part to 10 of water. Used to test for sulphates (R_2SO_4) .

Lime-water, Calcium Hydrate (CaO₂H₂). Slake a small lump of quicklime and shake up the slaked lime with water in a quart bottle and allow to stand twenty-four hours, filtering it into the reagent bottles from time to time. Used to test for carbonic acid (CO₂).

Potassium Ferrocyanide. "Yellow prussiate of potash." I part to 20 of water. Used to test for iron (Fe). Silver Nitrate (AgNO₃). I part to 20 of water. Used to test for chlorides (RCl).

Sodium Carbonate (Na_2CO_3). C.P. dry powder. Used to test for sulphates in dry way.

Sodium Phosphate (Na_2HPO_4) . 1 part to 10 of water. Used to test for magnesia (Mg).

Soap Solution. Such a quantity of white castile soap in 500 cc. of 70-per-cent. alcohol that 14.25 cc. of it gives the required lather with 50 cc. standard calcium chloride solution. This is equivalent to 0.10 gram of calcium carbonate. *Litmus Paper.* For testing for acids and alkalies. Acids turn blue litmus red; alkalies, red litmus blue. The deep blue color of the litmus should be reduced by exposure to the fumes of hydrochloric acid or with dilute acetic acid.

Tests for Various Elements and Compounds. — To gain familiarity with the appearance of the various precipitates which are characteristic of the element sought, the experiments described below may be performed. In each case we first make a solution containing a compound of the element sought, and then by suitable means or reagents throw down a precipitate or "sediment" which can only be thrown down when the element in question is present; or, instead of a precipitate, a color may be produced.

Test for Aluminum. Dissolve a piece of common alum half as big as a pea in one-third of a test-tube of water. Solids dissolve more readily when powdered, and when the water is warm; therefore in this case the alum may be ground in the mortar, and the test-tube of water warmed in the alcohol or gas-lamp flame. Or, since alum is only a compound of the metal aluminum for which we are testing, some aluminum filings or clippings — that quantity which could be retained on the tip of the small blade of an ordinary knife, may be dissolved or "cut" with hydrochloric acid about one-sixth to one-fourth of a test-tubeful.

Now add to the solution in a fine stream, and then drop by drop, some ammonia water, at last putting the thumb over the mouth of the tube and shaking it until the odor of ammonia is faintly perceptible. The

ammonia is now said to be "in excess." A whitish flocculent or gelatinous precipitate appears, which can be collected together on heating and filtered off for closer inspection if desired. For the method of folding the filter see under "Filters" and "Funnels" on page 23. The funnel may be supported by being set into the test-tube to receive the filtrate. Under these circumstances the precipitate (ppt.) is aluminum hydrate, and when a precipitate like this is obtained in testing a substance the composition of which is unknown, aluminum can be said to be present. Oftentimes "confirmatory tests" are used to substantiate or confirm these tests, or to make sure that the precipitate formed is really that produced by the element sought. In a case of this kind some of the precipitate on the filter is transferred, by means of a knife-blade or celluloid paper-cutter, to a piece of charcoal and heated in the oxidizing flame of the blowpipe; it gradually falls to a white powder, alumina. This is moistened with a few drops of 10-per-cent. solution of nitrate of cobalt, and again heated before the blowpipe. In the presence of alumina a fine blue color, resembling that seen on the "blue willow ware" of our grandmothers, is produced. The aluminum is present in the solution either as sulphate (alum) or aluminum chloride (AlCl₃), made by dissolving the aluminum in hydrochloric acid.

 $_2Al + _{6HCl} = _{2AlCl_3} + _{3H_2}$ aluminum + hydrochloric acid = aluminum chloride + hydrogen.

When to this solution of aluminum chloride, ammonia water (ammonium hydrate) is added, a simple interchange takes place between them and aluminum hydrate (the precipitate) and ammonium chloride are formed. This is shown in the reaction:

 $AlCl_3$ + $_{3}NH_4OH$ = AlO_3H_3 + aluminum chloride + ammonium hydrate = aluminum hydrate +

3NH₄Cl ammonium chloride

That this reaction would take place can be predicted by the fact that a precipitate (aluminum hydrate) can be formed. We can foretell with reasonable certainty that a reaction will take place if either a precipitate can be formed or a gas liberated under the conditions of the experiment.

Test for Calcium or "Lime." Dissolve a piece of chalk or marble as large as half a pea, or the equivalent amount of egg- or oyster-shell in a teaspoonful of hydrochloric acid (1 part strong acid to 3 of water). When the bubbling has ceased, make alkaline with ammonia. That is, add ammonia until on shaking and blowing out the vapors in the tube the odor of ammonia persists, that is, can be smelled faintly. Instead of relying on the sense of smell, red litmus paper may be used. When a drop of liquid is placed by means of a piece of glass tubing or glass rod on the reddened paper it turns back to the blue, and the liquid is said to have an alkaline reaction; or the paper may be dipped into the solution to be tested. After the solution is neutralized, as this process of adding ammonia is called, it is filtered into another test-tube to remove any undissolved chalk or shell and any precipitate formed by the ammonia water; the filtrate thus obtained is warmed (most precipitates forming best from warm solutions), and ammonium oxalate solution (see "Reagents") added, when a copious white precipitate of calcium oxalate comes down, which is evidence of the presence of calcium or "lime." In case only a very small quantity of calcium was present, twenty-four hours might be necessary for the formation of the precipitate, which would manifest itself by the appearance of a faint cloudiness on shaking the tube.

Test for Magnesium. Dissolve ten or a dozen crystals — more or less — of Epsom salts in one-fourth of a test-tube of water; add about 20 drops of ammonium chloride, and ammonia water to fill the tube nearly half-full and about a half-teaspoonful sodium phosphate solution. *Exact* quantities in this qualitative work are of little importance. A white crystalline precipitate of the double phosphate of ammonium and magnesium will appear, gradually increasing in quantity, which may require twelve hours for complete precipitation.

Test for Iron. Dip an iron wire for a few seconds into dilute hydrochloric acid, or dissolve one iron filing in this acid; add a drop of nitric acid and heat toboiling, cool, and add a few drops of potassium ferrocyanide: the precipitate or color is ferric ferrocyanide or Prussian blue.

Test for Sulphates. Make a solution of alum as in testing for aluminum; add a few drops of hydrochloric acid, and test the solution with litmus paper as has already been explained; now add some barium chloride solution and a dense white precipitate of barium sulUNIVERSITY

phate is produced. In testing for sulphates the solution must be always acid, with nitric or hydrochloric acid; or else other acids, as carbonic and oxalic, will be precipitated on the addition of barium chloride.

Test for Chlorides. Make a solution of common salt as directed for alum; acidify with pure nitric acid that is, add a few drops of acid — testing for acid with litmus as above, and add a few drops of silver nitrate solution: a white curdy precipitate of silver chloride is produced. This turns violet on exposure to light and dissolves in ammonia water.

To Test for Lime (Calcium) Salts in Boiler Water.---In the solutions for the above tests there has been present a considerable quantity of the substance which we have been testing for; that is, the solutions have been moderately strong. In boiler waters there may be only a few grains of solid matter per gallon, or, as more usually expressed, parts per million, and in order to get a prompt and characteristic reaction it is necessary to make a more concentrated solution by boiling off some of the water. Boil down in a porcelain dish 100 or 200 cc, of the water with the addition of a few drops of pure hydrochloric acid, until about one-tenth of the original quantity of water is left. Make alkaline with ammonia, filter and add ammonium oxalate to the filtrate, and if much lime be present a precipitate will appear: traces may require twenty-four hours for appearance.

To Test for Sulphates in Boiler Water. — Evaporate as above, using an alcohol lamp, as gas or gasolene contains sulphur enough to vitiate the test, and filter. Instead of adding ammonia, add barium chloride, when, if sulphate be present, the white barium sulphate will come down: traces may require twenty-four hours for appearance.

To Test Boiler Scale .- The sulphates of aluminum, calcium, etc., with which we have been dealing have all been in solution; and in case we had to deal with a solid substance — for example a boiler scale — the first thing to be done is to make a solution. To this end the scale is broken up fine and boiled with hydrochloric acid in a test-tube or porcelain dish. That which does not dissolve is probably sand. The solution in the dish is evaporated to dryness and ignited to render any dissolved silica or sand insoluble; it is treated with dilute hydrochloric acid, which dissolves everything but the silica, and the latter is filtered off. The solution is rendered faintly alkaline with ammonia when a reddish brown flocculent precipitate falls. This is filtered off; a quantity of the precipitate equal to half a pea is mixed with soda, and fused on a piece of platinum-foil over the lamp flame. The foil is placed in a porcelain dish and boiled with water, and the solution filtered. The iron contained in the scale is left on the filter as iron oxide; and any alumina (clayey material) goes into solution, by the fusion with soda. This is acidified with hydrochloric acid (that is, acid is added until the solution reddens litmus paper) and rendered faintly alkaline with ammonia, when, if alumina be present, it appears as a white flocculent precipitate. A small part of the reddish brown flocculent precipitate is dissolved in hydrochloric acid by heat-

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ing, diluted with water and a few drops of potassium ferrocyanide added, when a blue color or precipitate of Prussian blue appears, indicating the presence of iron.

To the liquid which has come from the filter containing the reddish brown precipitate, "the filtrate" as it is called, a half-teaspoonful of ammonium chloride is added and then ammonium oxalate until no further precipitation occurs: a dense white precipitate appears which is proof of the presence of "lime" or calcium. This is allowed to stand in a warm place for a day, is then filtered off, ammonia equal to about onethird the volume of the solution being added, using a beaker to hold it if necessary, and about a half-teaspoonful of sodium phosphate also added. In case much magnesia or magnesium compound is present, a crystalline precipitate appears. For small quantities it should be allowed to stand over night.

We have found by this analysis all the bases, iron, alumina, lime and magnesia, and one of the acids silicic or silica. The remainder of the acids must now be sought. On dissolving a scale in acid a bubbling takes place, and an odorless gas is given off. This gas is so heavy that it can be poured out of the tube into another and shaken up with lime water, giving a white precipitate showing the gas to be carbonic acid. A portion of the clear liquid is treated with a few drops of barium chloride, when a white precipitate of barium sulphate falls, indicative of the presence of a sulphate. The acids found are, then, carbonic, silicic, and sulphuric, and the scale may contain calcium carbonate and sulphate, magnesium carbonate, clay, aluminum silicate, iron rust, and possibly sand. The exact composition can be told only by a quantitative analysis. In performing a qualitative analysis an idea of the composition of the substance under examination may be obtained by observing the bulk of the precipitates formed. The analysis here described must be followed carefully as directed; otherwise the conclusions drawn will be worthless, as the precipitates obtained will not be those of the elements mentioned.

The scheme detailed applies only to substances that contain none of the commonly occurring metals except iron; and it has been given to show how an analysis is performed. Silver, lead, copper, zinc, tin, etc., have not been considered, as these, equally with the reasons for all the steps taken in the analysis cited, would take us beyond the limit of the present work. After completing a course in chemistry like that in Roscoe, or Storer and Lindsay, with experiments, the subject of qualitative analysis can be taken up, using the book of Eliot and Storer, revised by Lindsay, or that of A. A. Noyes. Ш

FUELS AND THEIR ANALYSIS

ANYTHING that unites with oxygen with the evolution of light and particularly heat might be used as a fuel. Of these substances few exist in sufficient quantity or are sufficiently cheap to be used as such. According to their physical condition they may be classed as solid, liquid, and gaseous. The solid fuels are wood and peat, or those of recent origin; brown, bituminous and anthracite coal, or fossil fuels; wood and peat, charcoal and coke, or modified fuels; and sawdust, spent tan, bagasse, etc., or refuse fuels. The liquid fuels are crude petroleum, substances derived therefrom, and various tarry residues from processes of distillation, as "dead oils." The gaseous fuels are natural gas, producer, blast-furnace, coke-oven, and illuminating gases.

The *essential* constituents in all these are carbon and hydrogen; the *accessory*, nitrogen, oxygen, water, and ash; and the *barmful*, sulphur and phosphorus.

The amount of the accessory or harmful constituents determines the values of these materials as fuels; obviously, those which contain the smaller quantity of these substances are to be preferred. In addition to this, the fusibility of the ash is to be considered: this should be as high as possible as the temperature developed, as the fused ash forms clinkers which stop up the spaces between the grate bars, rendering the access of air difficult or finally cutting it off altogether. These clinkers may in addition corrode the grates.

Solid Fuels

Wood. — Considering these various fuels, we find that wood is mainly woody fiber or cellulose, as the chemist calls it. This is seen in a practically pure condition in bleached cloth or absorbent cotton. It is formed from the carbonic acid and moisture in the atmosphere by the action of the green coloring matter (chlorophyl) of plants; carbonic acid + moisture = cellulose + oxygen. The plants absorb the carbonic acid which the animals give off and furnish the oxygen necessary for the sustenance of the latter. For fuel or timber, wood should be cut when it contains the least sap, that is, in the winter when the sap is in the roots: the percentage of water in wood varies from 30 per cent. in ash to 50 per cent. in poplar. The heavy hard woods, as maple and oak, make the best fuel, a cord of seasoned wood being about equal to a ton of coal, whereas of the soft woods, as pine and spruce, double this quantity is required. In a boiler test the "coal equivalent of kindling wood" used is usually found by multiplying the weight of the wood by 0.4. The ash of wood is mainly potassium carbonate — potash or pearlash.

The percentage composition of wood is about as follows:

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FUELS AND THEIR ANALYSIS

Water	Carbon	Hydrogen	Oxygen	Ash	Sp. Gr.
20	39	4.4	35.6	I	0.5

When burned it evolves from 7000 to 9000 B.t.u. per pound and requires about 6 pounds, or 74.1 cubic feet, of air for its combustion.

Peat is the compacted roots and stems of certain marsh plants, more particularly the mosses, which have undergone a slow decay under water. The process is supposed to resemble the first stage of the production of coal, marsh gas (methane) and carbonic acid being evolved.

It contains 10 per cent. of moisture even when "thoroughly dry"; this may vary from 20 to 50 per cent. in air-dried specimens. Nearly one-third of the available heat is employed in driving off this moisture. Its fuel value is further diminished by the high content of ash, which varies from 3 to 30 per cent., averaging 15 per cent.

In its natural condition, peat finds little use as a fuel in this country; it is, however, shredded and washed, whereby much of the sand and earth is separated. Oftentimes the peat is sufficiently free from mineral matter so that the washing may be omitted. It is then compressed into cylindrical blocks about two inches in diameter which are used for domestic purposes and are particularly well adapted for conditions where a fuel free from sulphur and phosphorus is essential. In Sweden alone two million tons of peat briquets are used yearly. In Russia peat impregnated with petroleum residuum, "petrolized peat," is used. The percentage composition of peat is approximately:

Water Carbon Hydrogen Oxygen Nitrogen Ash Sp. Gr. German 16.4 41.0 4.3 23.8 2.6 11.0 1.051 American 20.8 40.8 4.4 26.6 7.7 The heating value is about the same as wood, and practically the same amount of air is required for its combustion. The heating value of the compressed peat, or peat briquets (or brikettes), is not far from 8400 B.t.u. per pound, or about 60 per cent. that of ordinary soft coal

Coal. — Geologists tell us that coal was probably produced by the decay under fresh water of plants belonging principally to the Conifer, Fern and Palm families; these flourished during the Carboniferous Age to an extent which they never approached before or since. Representatives of the last family, which it is thought produced most of the coal, have been found 2 to 4 feet in diameter and 80 feet in hight.

By their decay, carbon dioxide, "choke-damp," marsh-gas, "fire-damp," and water were evolved. The change might be represented by the equation

 $\begin{array}{l} 6C_{6}H_{10}O_{5}=7CO_{2}+\ _{3}CH_{4}+14H_{2}O+C_{26}H_{20}O_{2}\\ Cellulose & Bituminous \ Coal \end{array}$

Some idea of the density of the vegetation and the time required may be obtained from the fact that it has been calculated that 100 tons of vegetable matter the amount produced per acre per century — if compressed to the specific gravity of coal and spread over an acre would give a layer less than 0.6 of an inch

¹ Taken from Gill, "Gas and Fuel Analysis for Engineers," by permission of the publishers, John Wiley & Sons, New York.

thick. Now four-fifths of this is lost in the evolution of the gaseous products, giving as a result an accumulation of *one-eighth of an inch per century*, or one foot in 10,000 years.¹

Brown Coal or Lignite may be regarded as forming the link between wood and coal; geologically speaking it is of later date than the true coal. Most of the coal west of the Rocky Mountains is of this variety.

As its name denotes, it generally is of brown color although the western coal is black — and has a conchoidal fracture. It contains a large quantity of water when first mined, as much as 60 per cent., and when "air-dry" from 15 to 20 per cent. The percentage of ash is also high, from 1 to 20 per cent.

The percentage composition of brown coal may be considered as approximately:

Water Carbon Hydrogen Oxygen and Nitrogen Ash Sp. Gr. German 18.0 50.9 4.6 16.3 10.2 1.3 Bituminous Coal. This is the variety from which all the following coals are supposed to have been formed, by a process of natural distillation combined with pressure. According to the completeness of this process we have specimens which contain widely differing quantities of volatile matter. This forms the true basis for the distinguishing of the varieties of coal. In ordinary bituminous coal this volatile matter amounts to 30 or 40 per cent. Three varieties of bituminous coal are ordinarily distinguished, as follows:

¹ In case the reader desires to follow in a more extended manner the geology of coal, reference may be had to Le Conte's "Elements of Geology," pages 345-414, 3d ed.

Dry or non-caking — those which burn freely with but little smoke and, as the name denotes, do not cake together when burned. The coals from Wyoming are examples of this class.

Caking — those which produce some smoke, and cake or sinter together in the furnace. Examples of these are the New River and Connellsville coals.

Fat or long-flaming — those producing much flame and smoke and which do or do not cake in burning; volatile matter 50 per cent. or more. Some of the Nova Scotia coals belong to this class.

Bituminous coal varies much in its composition, is black or brownish black, soft, friable, lustrous, and of specific gravity of 1.25 to 1.5. Moisture varies from 0.25 to 8 per cent., averaging about 5.

The percentage composition of bituminous coal may be considered as approximately: ¹

Water	Carbon	Hydrogen	Oxygen	Nitrogen	Ash	Sulphur
0.9	77 . I	5.2	6.7	1.6	7.6	1.0
	Water	Volatile M	atter Fix	Fixed Carbon		
	0.9	27.4		64.1	7.6	

Semi-Bituminous or Semi-Anthracite Coal is upon the border-line between the preceding and the following variety; it is harder than bituminous, contains less volatile matter (15 to 20 per cent.), and burns with a shorterflame. An example of this is the Pocahontas coal.

The percentage composition of semi-bituminous and semi-anthracite coal may be considered to be approximately: ¹

¹ H. J. Williams.

Water	Carbon	Hydrogen	Oxygen	Nitrogen	Ash	Sulphur	
0.5	83.0	4.7	4.2	1.3	5.5	0.8	
Water		Volatile Matter		Fixed Carbon		Ash	
0.5		16.7		77.3		5.5	

Anthracite Coal is the hardest, most lustrous, and densest of all the varieties of coal, having a specific gravity of 1.3 to 1.75; it contains the most carbon and least hydrogen and volatile matter (5 to 10 per cent.). It has a vitreous fracture and kindles with difficulty, burning with a feeble flame, giving little or no smoke and an intense fire. The Lehigh coal is an excellent example of this class.

The percentage composition of anthracite coal may be considered as approximately: ¹

Water	Carbon	Hydrogen	Oxygen	Nitrogen	Ash	Sulphur
2.0	83.9	2.7	2.8	0.8	7.2	0.6
	Water	Volatile Ma	atter Fi	xed Carbon	As	h
	2.0	4.3		86.5	7-2	2

The ash of coal varies from 1 to 20 per cent., and is mainly clay — silicate of aluminum — with traces of lime, magnesia, and iron. When coal is burned it yields from 10,980 to 14,400 B.t.u. and requires about twelve times its weight of air, or 156.7 feet per pound. For the greatest economy Scheurer-Kestner found that this should be increased from 50 to 100 per cent.

The sizes of anthracite coal that are usually found on the market are:

Broken or furnace, that retained by a screen with meshes $2\frac{1}{2}$ inches apart.

¹ H. J. Williams.

Egg, that retained by $1\frac{3}{4}$ -in. mesh, passing $2\frac{1}{2}$ -in. Stove, that retained by $1\frac{1}{4}$ -in. mesh, passing $1\frac{3}{4}$ -in. Nut, that retained by $\frac{3}{4}$ -in. mesh, passing $1\frac{1}{4}$ -in. Pea, that retained by $\frac{1}{2}$ -in. mesh, passing $\frac{1}{4}$ -in.

Buckwheat, rice, barley, and culm are smaller sizes than $\frac{1}{4}$ -in. It is worthy of note that the smaller the coal the higher the percentage of ash, that in buckwheat being about 16 per cent. as against 5 per cent. in egg.

Coke is prepared by the distillation of bituminous coal in ovens. These are of two types: those in which



FIG. 15. — Otto-Hoffman Coke Oven. Longitudinal Section

the distillation products are allowed to escape, the "beehive" ovens; and those in which they are carefully saved, as the Otto-Hoffman, Semet-Solvay, Simon-Carvès and others. The "beehive" ovens yield from 50 to 65 per cent. of the weight of the coal used, about $2\frac{1}{2}$ tons. The Otto-Hoffman ovens, shown in longitudinal section, Fig. 15, in cross section, Fig. 16, and general perspective, Fig. 17, are long, narrow, thin-walled retorts 33 x 6 x 1.5 feet, regeneratively heated by side and bottom flues. The regenerative heating consists

in allowing the products of combustion to heat to a good red heat the chambers through which the gas and



Coke Oven. Cross Section

the air for its combustion pass. Two sets of these chambers are used alternately, usually half-hourly, one



FIG 17. — Otto-Hoffman Coke Oven. General Perspective

being heated by the products of combustion, while the gas and the air are being heated by the other set. Six

tons of coal make the charge, and the yields of byproducts are about as follows: Coke, 70 to 75; gas, 16 (10,000 cubic feet); tar, 3.3; ammonia, 0.3 to 1.4 per cent.

The Semet-Solvay ovens differ from the Otto-Hoffman in that their walls are thicker, serving to store up the heat. They also cost less for repairs and in leakage, and are not regeneratively heated; the yield of coke is higher, about 80 per cent. Fig. 18 shows a cross section of the oven.



FIG. 18. - Semet-Solvay Coke Oven

The analysis of Connellsville coke, with the coal from which it is prepared, is as follows:

W	Vater V	ol. Matter	Carbon	Sulphur	Ash
Coal 1	1.3	30.1	59.6	0.8	8.2
Coke c	0.03	I.3	89.2	0.084	9.5
		Fix	ed Carbo	n	
Otto-Hoffman Coke 3	3 · 7	I.3	86.1 .		8.9
Heating value 12,800	B.t.u.				

The Minor Solid Fuels. — As was said in the early part of this chapter, the efficiency of fuel, and particularly of the minor solid fuels, depends upon the amount

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of moisture which they contain. Sawdust and Logwood chips are employed as fuel to good advantage in special automatic furnaces; spent tan bark with 57 per cent. moisture gave an evaporation of 4 pounds of water per pound of bark.

Wheat straw finds application as a fuel in agricultural districts, $3\frac{1}{2}$ pounds being equal to one pound of coal. Upon sugar plantations the crushed cane or *bagasse*, partially dried, is extensively used as a fuel. With 16 per cent. of moisture it gave an evaporation of double its weight of water.

Briquets, "Patent Fuel." In Europe coal dust is cemented together with some tarry binding material, baked or compressed into blocks usually about 6x2x1inch, and used as a fuel. In some cases they take the form and size of a large goose egg, and are called eggettes.¹

STORAGE OF COAL AND SPONTANEOUS COMBUSTION

While authorities differ as to the way and manner in which coal should be stored, as regards hight of pile, number, size and arrangement of ventilating channels, they are practically agreed that it should always be covered. Six months' exposure to the weather may cause a loss of from 10 to 40 per cent. in heating value. The North German Lloyd Steamship Company stores its coal in a covered bin provided with ventilators, and restricts the hight of the pile to 8 feet. A large gas company in a Western city also uses a covered bin,

¹ These are now being made at Scranton, Pa.

with ventilators 8 inches square every 20 feet; the hight of the pile may be from 10 to 15 feet.¹ Ventilating flues serve the additional purposes of enabling the temperature of the pile to be ascertained before ignition sets in, and as a means of introduction of either steam or carbonic acid to extinguish any fire which may occur. All the supports of the bin in contact with the coal should be of brick or iron, and if of hollow iron, filled with cement.

The spontaneous combustion of coal is due primarily to the rapid absorption of oxygen by the finely divided coal and to the oxidation of iron pyrites, "coal brasses," occurring in the coal. The conditions favorable to this process are: first, a supply of air sufficient to furnish oxygen, but of insufficient volume to carry off the heat generated; second, finely divided coal, presenting a large surface for the absorption of oxygen; third, a considerable percentage of volatile matter in the coal; and fourth, a high external temperature.

A good way to extinguish a fire in a coal pile not provided with ventilators consists in removing and spreading out the coal and flooding the burning part with water. Another method consists in driving a number of iron or steel pipes provided with "driven well points" at the place where combustion is taking place, and through these forcing water or steam upon the fire.

¹ A large electric company in that same city has arranged to store 14,000 tons of coal under water in 12 pits. A steam shovel is used to dig out the coal. (*Engineering and Mining Journal*, September 15, 1906.)

FUELS AND THEIR ANALYSIS

The table shows the composition and heating value of some American coals:

Proximate Analysis and Heating Value of $${\rm American}$$ Coals 1

Name	Moist- ure	Vol. Matter	Fixed Carbon	Ash	Sulphur	Heat Value per lb. B.t.u.
ANTHRACITE : Northern field	3.4	4.4	83.3	8.2	0.7	13160
Semi-anthracite: Loyalsock	1.3	8.1	83.3	6.2	1.6	13920
SEMI-BITUMINOUS: Clearfield, Pa. Pocahontas, Va. New River, W. Va.	0.8 1.0 0.8	22.5 21.0 17.9	71.8 74.4 77.6	4.0 3.0 3.4	0.9 0.6 0.3	14950 15070 15220
BITUMINOUS: Connellsville, Pa Pittsburg, Pa. Hocking Valley, Ohio Missouri	1.3 1.4 6.6 6.4	30.1 35.9 35.0 37.6	59.6 52.2 48.9 47.9	8.2 8.0 8.0 8.0	0.8 1.8 1.6	14050 13410 12130 12230
LIGNITES: Iowa Utah	8.4 9.3	37.I 42.0	35.6 44.4	18.9 3.2	 I.2	8720 11030

¹ Taken from "Steam," published by the Babcock & Wilcox Co.

ANALYSIS OF SOLID FUELS

Sampling.¹ In sampling from cars proceed as follows: Beginning at one corner of the car, drive a scoop shovel vertically down as deep as it will reach. Bring it out with all the coal it will hold and throw it into a cart or wheelbarrow. Repeat, taking six scoopfuls along one side of the car, at equal intervals, six through the center and six along the other side. Place the coal taken, on a close tight floor, and break all the lumps larger than an orange. Mix by shoveling it over on itself, back and forth, quarter and reject opposite quarters. Break finer, as may be necessary, and continue to quarter down until a sample is obtained small enough to go into a quart fruit jar and having no larger than 1-in. cube. The sample may, with advantage, be run rapidly through a mill which will break it into the size mentioned. Transfer it to the jar and make sure the latter is sealed air-tight before it is set aside. All of these operations should be conducted as rapidly as possible, to guard against any change in the moisture content of the coal.

Possibly a more representative sample may be obtained by taking shovelfuls of the coal at regular intervals during the loading or unloading of the car. In boiler tests shovelfuls of coal should be taken at regular intervals and put into a *tightly covered* barrel or receptacle and placed where it is protected from the heat of the furnace. In sampling, two conditions must be rigidly observed: first, the original sample

¹ From the report of the Committee on Coal Analysis, Journal American Chemical Society, xxi (1899), 1116. should be of considerable size and thoroughly representative; and second, the quartering down to an amount which can be put into a sealed jar should be carried out as quickly as possible after the sample is taken. Shipment in wooden receptacles should not take place with coals containing more than 2 per cent. of moisture.

For the analysis, quarter down the sample in the jar further to about 3 ounces — a good handful; run this quickly through a coffee mill set to grind as finely as possible, and transfer a portion of this to a tightly stoppered test-tube for use in determining moisture. Grind about half an ounce of the remainder moderately fine in a porcelain or iron mortar, transfer to a tightly corked tube for use in other determinations. Careful samplings and careful treatment of samples are necessary to obtain reliable results, especially in the determination of moisture. A car-load of many Western coals may lose several hundred pounds of moisture daily while standing on the track, and the same coal may lose several per cent. of moisture by standing for a few days or weeks in a loosely stoppered bottle.

The methods employed in the analysis of fuels are largely a matter of convention, various methods giving varied results; for example, it is well-nigh impossible to obtain accurately the percentage of moisture in coal, as when heated sufficiently hot to expel all the moisture, some of the hydrocarbons are volatilized.

Moisture. Conventional method: Dry one gram of coal in an open crucible at 220 to 225 deg. F. (104 to 107 deg. C.) for one hour.

Another method: Procure a pair of 3-in. watch

glasses, the edges of which are ground to fit accurately together and which are held together by a watch-glass clip. Weigh out about 5 grams of the coal from the test-tube mentioned above, between these glasses, using the horn pan balances.

Remove the clip, open the glasses and place them in the oven at 220 to 225 deg. F. (104 to 107 deg. C.) for one hour; remove them from the oven, replace the clip, cool under a bell jar and weigh them cold. The loss of weight represents the moisture in the coal and should be expressed in per cent.

The conventional method of drying one gram of coal in an open crucible at the above temperature cannot be used unless an analytical balance sensitive to milligrams is at hand. The method outlined gives results closely agreeing with the latter.

Volatile Combustible Matter, Coke, and Ash. These determinations cannot be carried out with sufficient accuracy using the horn pan balances; also a gas-burner for heating the coal is essential.

The method consists in heating one gram of coal with a flame of definite size for a definite length of time in a platinum crucible.¹ Professor Parr² recommends a porcelain crucible in a special furnace.

These are all the determinations that it is possible to perform with the apparatus at hand and without careful training and considerable experience in the handling of delicate apparatus. The other determinations involved will be briefly described.

¹ Gill, "Gas and Fuel Analysis for Engineers."

² Parr, "The Coals of Illinois." University of Illinois Bulletin, vol. 1, No. 20.

Carbon and Hydrogen. Carbon exists in coal probably in the free condition and also combined with hydrogen. These elements are determined by burning the coal in a stream of air or oxygen freed from carbonic acid and moisture; the carbon burns to carbonic acid and the hydrogen to water, both of which are absorbed in suitable chemicals contained in weighed tubes and bulbs. From their increase in weight the weights of these gaseous products are found, from which the weights of carbon and hydrogen can be obtained and the percentages of these constituents calculated. Parr¹ dissolves in water, in a flask, the residue from the determination of heating power in his calorimeter, acidifies, liberating the carbonic acid, and measures it, from which he can determine the total carbon in the coal.

Nitrogen is determined by Kjeldahl's method, by which the nitrogeneous bodies in coal are changed to ammonia by digestion with strong sulphuric acid and potassium permanganate. By distilling the residue treated with soda, the ammonia is liberated, caught in acid of definite strength, and thus its quantity determined.

Sulphur is estimated by heating the coal with a mixture of magnesia and soda, cooling, and burning the coal by igniting with ammonium nitrate. The resulting mass is dissolved in hydrochloric acid and the sulphuric acid, into which the sulphur compounds in the coal have been changed, estimated by precipitation with barium chloride in the usual way. Parr¹ uses the residue from the combustion in his calorimeter

¹ Parr, "The Coals of Illinois." University of Illinois Bulletin, vol. 1, No. 20.

for the determination of sulphur. Instead of weighing the barium sulphate precipitated, it is estimated photometrically.

Oxygen is determined by adding the percentage of carbon, hydrogen, ash, nitrogen, sulphur, and moisture together and subtracting their sum from 100; there is no method for its direct determination.



FIG. 19.— William Thomson's Calorimeter

DETERMINATION OF THE CALORIFIC POWER OF SOLID AND LIQUID FUEL

A. Direct Methods. — Many forms of apparatus have been proposed for this purpose. With the exception of those employing Berthelot's principle — of burning the substance in a bomb under a high pressure of oxygen — few have yielded satisfactory results.

William Thomson's (Fig. 19) and Barrus's calori-

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meter (Fig. 20), in which the coal is burned in a bell jar of oxygen, usually yield results as much as 3 per cent. from the real value, obtained by the Mahler bomb, and they may be 8 per cent. from the truth.



FIG. 20. — Barrus's Calorimeter

Furthermore, it is not easy to burn certain anthracite and semi-bituminous coals in this type of apparatus.

Lewis Thompson's calorimeter (Fig. 21), in which the coal is burnt in a bell jar by oxygen furnished by the decomposition of potassium chlorate or nitrate, gives results which must be increased by about 15 per cent.

Parr's calorimeter (Fig. 22) employs the same principle as the preceding, but possesses the advantage that no gases are evolved from it as in all the foregoing forms, which carry off heat in bubbling through the water. It gives results well within 0.5 per cent. of those obtained by the bomb calorimeter. In two cases which have come to the writer's notice it has ex-



FIG. 21. — Lewis Thompson's Calorimeter

ploded, scattering hot sodium peroxide about, causing painful and in one case serious burns.

Berthelot's, Mahler's, Williams's, or Norton's calorimeter (Fig. 23), is of the bomb type, constructed of mild steel or phosphor bronze and lined with platinum, enamel, or gold. The coal is burned under a pressure of 225 to 250 pounds of oxygen in this closed vessel provided with an electrical ignition. It gives results which with proper corrections are accurate, as all of the heat developed by the fuel is measured and the losses can be exactly determined.

All these apparatus are expensive and require experience in manipulation, and with the exception of



FIG. 22. - Parr's Calorimeter

the last two types give results no more nearly correct than the one about to be described.¹

Berthier's Method. This uses as a measure of the heating value the amount of lead which a fuel will reduce from the oxide; that is to say, the heating value is proportional to the amount of lead reduced or oxygen absorbed.

¹ Directions for their use as well as a more detailed description will be found in "Gas and Fuel Analysis for Engineers"; also Poole's "Calorific Power of Fuels." One gram of the finely powdered dry coal is carefully weighed out on the horn pan scales and intimately mixed with 60 grams of common litharge (oxide of lead) and 10 grams of ground glass. This mixing can be done with a palette knife on a sheet of glazed paper. The mixture is transferred to a clay crucible of the size of Battersea C, covered with a layer of salt, the crucible



FIG. 23. - Norton's Calorimeter

covered and heated to redness in the hottest part of the boiler furnace for fifteen to twenty minutes. The crucible is cooled, then broken, the lead button carefully cleansed from the adhering slag and weighed on the scales.

The number of grams of lead obtained, reduced to the basis of that obtained from one gram of coal, in case exactly one gram of coal was not used, multiplied by 483 gives the number of B.t.u. that will be yielded by one pound of coal. An example will make this clear.

> Weight of coal taken, 1.04 grams. Weight of lead button, 31.84 grams. $31.84 \div 1.04 = 30.62, \times 483 = 14,750$ B.t.u.

Two other experiments gave 14,500 and 14,550 B.t.u. The same coal gave in the Mahler-Norton bomb, 14,200 B.t.u., or 2.8 per cent. lower, which it will be observed is as close as any calorimeter gives, excepting Parr's.

B. By Calculation. - In case the chemical analysis of the coal be given, its heating value can be found by calculation. This depends upon the principle that the heating value of a substance is the sum of the heating values of its constituents. If we could determine the heating value of the carbon and hydrogen contained in the coal, these values multiplied by the percentage of these elements in the coal would give the heating value. As we have but a faint idea of the way in which carbon and hydrogen occur in coal, their exact heating values cannot be determined, and in their stead the values obtained by burning charcoal and pure hydrogen are employed. Inasmuch as hydrogen combines with eight times its weight of oxygen, the oxygen in the coal is considered to render inert the hydrogen in the coal corresponding to eight times the weight of oxygen, and this is subtracted from the percentage of hydrogen, giving the percentage of hydrogen actually available as fuel.

The following formula is found to give results in

B.t.u. within about 3 per cent. of those obtained in the bomb calorimeter:

$$\frac{14540c + 51840 (h - \frac{o}{8}) - 1080w}{100}$$

In case the percentage of sulphur exceeds 2, this should be taken into consideration, by the introduction of 4500s into the numerator. *c*, *b*, *o*, *s*, and *w* represent respectively the percentages of carbon, hydrogen, oxygen, sulphur, and water contained in the coal. The water formed by the combustion of hydrogen is considered to be in the vaporous condition.

The results obtained by these formulas, while reasonably correct for bituminous coal, for anthracite coal are, as a rule, considerably too low.

Goutal has proposed the formula:

Heating value =
$$\frac{14670c + A \times M}{100}$$

c here represents the percentage of fixed carbon (coke - ash); M the percentage of volatile matter 100 - (coke + ash + water) and A is a coefficient which varies with the amount of volatile matter M as follows:

M = 2 to 15	A = 23400
15 to 30	18000
30 to 35	17100
35 to 40	16200

The results upon a series of American coals varied less than 2 per cent. from those obtained by the bomb calorimeter.

LIQUID FUELS

These consist of petroleum and its products and various tarry residues from processes of distillation, as

from petroleum, coking ovens, wood and shale. The advantages of liquid fuel are its increased heating power, the decreased labor employed in its use, and its ease of manipulation. The burners oftentimes require no change for a day at a time, and there being no fire doors to open, the inrush of cold air, causing strains in the boiler, is obviated. Not the least of its advantages are its cleanliness and freedom from smoke, cinders, and ash. Owing to the increase in heating power the boiler can be smaller and do the same work.

The origin and obtaining of petroleum will be described in Chapter VI.

Crude petroleum varies greatly in color according to the locality. It is usually yellowish, greenish, or reddish brown, of benzine-like odor, and specific gravity of 0.78 to 0.80. It "flashes" at the ordinary temperature; hence great care should be employed in its use and storage. Its percentage composition is shown below:

Carbon	Hydrogen		
84 to 85	16 to 15		

It is more than twice as efficient as the best anthracite coal, giving in practice an evaporation of 14 to 16 pounds of water per pound of petroleum, or an efficiency of 19,000 B.t.u. as against 8500 B.t.u. for anthracite. In general, $3\frac{1}{2}$ to 4 barrels of oil, of 50 gallons, are equivalent to a ton of good soft coal.

The various **tarry residues** would probably not differ materially from Russian petroleum residues, which have an evaporating power of about 13 pounds of water per pound of residue. The only two tests that it is important to make upon liquid fuels are the *flash test* described in the chapter upon oil, page 150, and *heating value*, for which the Junkers' gas calorimeter may be used, which is described in "Gas and Fuel Analysis for Engineers." The bomb calorimeter, or Parr's, may also be used. The flash test, which should at least be as high as that of kerosene oil, about 100 deg. F., is important as indicating the degree of safety of the oil when handling it.

The table shows the heating values and some other constants of some liquid fuels.

	Sp. Gr.	Flash, Deg.F.	Fire, Deg.F.	Heat Val. B.t.u. per lb.	Sp. Heat
76° B. Naphtha ¹	76.5° B.	_		18080	0.55
62° B. Naphtha ¹	61.0	_		17860	0.50
135° F. Fire T. Kerosene ¹	48.0	125	135	17810	0.50
150° F. Fire T. Kerosene ¹	48.0	134	150	18290	0.49
Beaumont Crude ²	0.924	180	200	19060	
California ²	0.966	230	311	18667	
California and Texas ²	0.966	270	280	19215	
Pennsylvania ³	0.886			19224	
Wyoming ³	0.996	-		19668	
Residuum, Va. ³	0.860			19200	
Residuum, Russian ³	0.884	—		10926	

¹ Gill and Healey, *Technology Quarterly*, xv (1002), 74. ² Report U. S. Naval "Liquid Fuel" Board (1904).

³ Poole, "The Calorific Power of Fuels" (1898).

Gaseous Fuels

The use of gaseous fuel, although finding application only of late years, dates back a full century. Lampadius, in Freiberg in 1801, utilized the waste gases from the carbonization of wood, and Aubertot, in 1811, those from the blast furnace. It is, however, to the labors of du Faur, in Würtemberg in 1837, that the present extended use of gaseous fuel is largely due. Gaseous fuel is of three different types: 1. Natural gas. 2. Producer and blast furnace gas. 3. Coal and water gas.

Natural gas is often obtained when boring for petroleum, or wells are especially drilled for it. It is mainly composed of methane or marsh gas, and hydrogen, the percentage varying with the locality.

Producer gas is made from hard or soft coal in a gas producer or generator, by blowing a stream of air up through a deep bed of fuel. The coal is first burned to carbonic acid and this is reduced to carbonic oxide by the upper layers of fuel. It is largely nitrogen with carbonic oxide and some hydrogen.

Gas producers are of two classes: (a) those in which a blast of air is blown up through them, usually by a jet of steam; and (b) suction producers, which are usually coupled directly to gas engines, in which the movement of the engine piston serves to suck air through the fuel.

(a) Producers with blast (pressure producers). Mond, Miller, Dowson, Siemens, Morgan, and Taylor are some of the inventors whose names are connected with this form of generators, of which the latter, shown in Fig. 24, may be taken as a type. This consists of a boiler-iron shell about 15 feet in hight and 10 feet in diameter, lined with firebrick. The grate is a solid iron plate



FIG. 24. — Taylor Gas Producer

which is rotated, thus permitting the ashes to be removed by forcing them against stationary iron rods. Peep holes through the walls give an idea of the hight to which the ashes rise. An automatic feeding device, a pipe for the steam-produced blast and an exit tube for the gases complete the apparatus. This construction embodies the conditions necessary for a successful gas producer, which are:¹

First, a continuous and automatic feed, which insures regular and uniform production of gas.

Second, a deep bed of fuel and a deep bed of ashes. A deep bed of fuel is essential for the reduction to carbonic oxide of the carbonic acid first formed; and a deep bed of ashes insures the combustion of all the coal.

Third, a level support for the fuel and ashes, which gives an even depth of fuel over the whole furnace. If the grate slants, the fuel is thicker at one point than another, producing consequently an uneven quality of gas.

Fourth, the blast is carried by a pipe nearly through the deep bed of ashes, which requires a lower pressure of steam and blast. Last, but not least, the hight to which the ashes rise is visible and they are easily removable through apertures provided for the purpose.

A producer of the size given will gasify $6\frac{1}{2}$ tons of anthracite pea coal or 8 tons of bituminous coal in twenty-four hours: about 170,000 cu. ft. of gas of 138 B.t.u. per cubic foot are produced per ton of anthracite coal, which corresponds to a conversion of about 85 per cent.

(b) Suction producers. In this type the movement of the gas-engine piston sucks the air necessary for gas-making through the bed of fuel. The gas passes through an economizer containing water, the steam of

¹ Based on "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., Philadelphia, Pa.



which is conducted beneath the producer grate and sucked up with the air. On leaving the economizer the gas goes to a coke scrubber, where it is sprayed with water to remove the dust and, if necessary, to a sawdust purifier and thence to the engine. A gas-holder is not needed, as with a pressure producer, although a regulator is often employed. For starting the producer a hand- or power-driven fan is employed.

It is claimed for gas producers that they require less space than a steam plant of equal size, and whereas the first cost and labor charges for installation are rather less than of steam, the running expense for labor, repairs, and maintenance are considerably less. A marked feature of a producer-gas plant is the readiness of operation and economy of fuel during hours of idleness. Another feature is the complete absence of smoke. It is further stated that with coal at \$2.50 to \$3.00 per ton producer gas costs at the furnaces or engines about 10 cents per 1000 cubic feet.

From anthracite coal at \$5 per ton, one brake horsepower per hour per pound of coal; can be obtained at a cost of 0.25 cent, with bituminous coal at \$2.50 per ton, one and a quarter pounds of coal are used, at a cost of 0.1565 cent per brake horse-power per hour.

Blast-furnace gas is the gas issuing from the top of an iron blast furnace, and is practically of the same composition as producer gas. It has been used to run gas engines at the Cockerill Company's works at Seraing, Belgium, and at the Lackawanna Steel Com-

pany's plant at Buffalo for a number of years with good success, in units of 200 to 2000 horse-power.

The calculation has been made that by using the gas from three blast furnaces a saving of \$150,000 per year in power could be made by the use of gas engines, at an outlay of \$500,000. The prediction is made that by the utilization of these gases for power purposes metallurgical plants may become important centers of power.

The analysis of these various gases is shown in the table below.

Coal Gas.—One method of the manufacture of coal gas has already been described under the heading coke, using there the Otto-Hoffman or Semet-Solvay by-products ovens. In addition to these, coal is distilled in D-shaped clay retorts, primarily for the purpose of making gas, — coke, tar, etc., being by-products. Coal gas is largely methane and hydrogen with small percentages of "illuminants" and carbonic oxide. Its illuminating power is from sixteen to nineteen candles.

Water Gas.—As its name denotes, a gas made from water by decomposing it with coal at a high temperature:

Coal + water = water gas Carbon + hydrogen oxide = carbonic oxide + hydrogen

If we pass steam, instead of air, —as in a producer, over hot coal, it is decomposed, giving carbonic oxide and hydrogen. From the flame it produces on burning, it is called "blue" water gas. To make it luminous and enable it to be used as an illuminant, it is enriched by blowing petroleum vapor into it, "gas oil," and

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passing the mixture through hot checker work, decomposing the vapor, or "fixing it," into permanent gases of high illuminating power. The illuminating power of enriched water gas is from twenty-five to twentyeight candles.

	Meth- thane	Hydro- gen	Illumi- nants	Carb. acid	Carb. oxide	Oxy- gen	Nitro- gen	B. t. u. pr. cu.ft.
Ohio	93.3	1.6	0.3	0.2	0.4	0.4	3.6	10201,2
vania	89.6	4.9	5.0	0.3	0.3	<u>. </u>	_	1073 ²
Producer pressure	_	12.0	-	2.5	27.0	0.3	57.0	145
Producer suction	0.5	18.5	_	8.0	26.0	-	47.0	145
Blast furnace	_	I.4	_	0.6	34.3	_	63.7	122
Coal Enriched	34.8	50.6	5.2	1.2	6.2	-	2.1	599 ²
water Blue	19.1	31.3	15.0	3.0	27.4	0.4	3.8	736 ²
water	0.8	52.4	-	4.6	41.5	-	0.5	332 ²
Wood	2.9	0.5	0.6	11.5	28.4	-	56.1	1452
Peat	2.7	0.9	• 4	12.1	27.2	_	56.7	138 ²

COMPOSITION OF SOME GASEOUS FUELS

1 0.2 per cent. hydrogen sulphide.

² From Poole, "The Calorific Power of Fuels."

IV

THE REGULATION OF COMBUSTION – GAS ANALYSIS

THE fuels themselves were treated of in the last chapter, and were it not for the fact that the appliances for their application would take us too far from our subject, these would be next discussed.¹

Before leaving the topic of the methods of burning coal, just a word should be said regarding the use of various chemicals mixed with or dissolved in water and sprinkled upon the coal, it being claimed that they aid combustion. Such are "Kem-Kem," "Koal Spar," "Koala Sava,"² "Fuel Savers," etc., which consist mainly of salt with a small percentage of something furnishing oxygen at a high heat, as saltpeter. One of these compounds ² was of the following composition: 2000 lb. salt, 100 lb. copperas, 25 lb. charcoal, 15 lb. niter, and 15 lb. cooking soda. Three pounds of this

¹ These will be found described at length in : Groves and Thorp, "Chemical Technology," vol. i; Mills and Rowan, "Fuels " (1880); Barr, "Boilers and Furnaces"; Christie, in *Engineering Magazine*, xxiii (1902), 528, 717; E. A. B. Hodgetts, "Liquid Fuels"; Report of the U. S. Naval "Liquid Fuel" Board, Washington, 1904; Williston, in *Engineering Magazine*, xxiv (1903), 237; Professional Paper No. 48: Report on the Operations of the Coal-Testing Plant of the U. S. Geological Survey at St. Louis, 1904, parts I, II, and III, Washington, 1906; also "Gas Producers," and "Gas Fuel," circulars of R. D. Wood & Co., Philadelphia, Pa.

² Journal Society Chemical Industry, xxi (1902), 330.

was to be "dissolved" in water and sprinkled on a ton of coal. Used in this way, about one-third of an ounce of niter would be furnished per ton of coal, which would yield about three pints of oxygen gas. As 210 cu. ft. of air are required per *pound* of coal, or 420,000 cu. ft. per ton, the effect of these three pints of oxygen in this quantity of air can be easily imagined.

Some of these compounds have even been patented, and of this the eminent German engineer, Professor Ferdinand Fischer, says: "Such nonsense should not be patentable."¹ In a test which came to the writer's notice no gain could be seen by the use of these compounds.

Combustion is usually regulated by a more or less arbitrary opening and closing of the dampers or by damper regulators. It is more and more coming to be governed by an examination of the "smoke gases," as they are called, or the chimney gases. This may be done either by occasional chemical analysis or by certain automatic apparatus which are in operation continuously.

A. Examination of Chimney Gases by Chemical Analysis

To this end a sample of the gases must be drawn from the chimney into the gas apparatus where the various components are determined.

Sampling Apparatus. A glass tube $\frac{5}{8}$ in. in diameter and about three feet long, drawn down to $\frac{1}{4}$ in. at one

¹ Solcher Unsinn sollte nicht patentirbar sein.

end, is inserted into the uptake or smoke-pipe leading to the chimney, on the grate side of the damper. For this purpose a $\frac{3}{4}$ -in. hole is drilled into this duct or pipe, and the space around the tube stopped with putty, plaster of Paris, or wet cotton waste. The tube should be inserted for about half its length, and the place chosen for its insertion should be as near the point where the gases leave the boiler as possible, so that a representative sample may be secured. The object in this is to prevent the contamination of the combustion gases by leakage of air through cracks in the clean-out doors and setting, and also where the damper is fitted: all these places should be plastered up, as the leakage through them or even through a brick wall is not inconsiderable. In some cases it will be found that the draft is materially increased by the sizing and whitewashing of the boiler setting. In making a test of chimney gases all openings other than the legitimate ones for draft should be carefully closed. It is well also to place in the tube two rolls of fine wire gauze three inches long, to strain out the soot.

Some means of sucking out the sample of gas must now be provided. Where samples are taken infrequently, an ordinary double-ended rubber syringe bulb, provided with suitable hard-rubber valves, may be used. Better than this, and possessing the advantages of permanency, and ease and rapidity of operation, is some form of water-jet pump as the Richards (Fig. 25) or Chapman's; these are constructed and operate like the familiar boiler injector; and, if water be inconvenient of access, steam may be used instead. A piece of $\frac{1}{4}$ -in. rubber tubing is connected to the air intake and the tubing attached to the sampling tube in the flue. Where long runs of tubing are needed it will be found cheaper to employ $\frac{1}{4}$ -in. lead pipe, using short pieces of rubber tubing to give flexibility to the connections. As few rubber connections as possible should be used, as they deteriorate and give rise to





leaks. "Cup joints" made with soldering-iron are to be preferred. A lead T with a rubber connector and pinch-cock connecting with the gas analytical apparatus is inserted in the rubber tubing and we are ready to take a sample of chimney gas. The arrangement of the apparatus is shown in Fig. 25.

To take a sample of gas the pump is started and a

stream of gas sucked out from the chimney down into the pump. The burette in the gas apparatus having been filled with water, the pinch-cock a is opened and enough gas sucked into the burette to displace any air in the stem of the T-tube and its connections. This is expelled by pinching the rubber connector, thereby making a channel in it through which finally the confining water drips. The gas is sucked in again until rather more than 100 cc. are brought into the burette.

GAS ANALYTICAL APPARATUS

In the writer's opinion ¹ the apparatus which is best adapted for this purpose is that of Orsat: it is readily portable, not liable to be broken, easy to manipulate, sufficiently accurate, and, in the modification about to be described, always ready for use, there being no stop-cocks to stick fast.

Orsat Apparatus. — Description. The apparatus (Fig. 26) is enclosed in a case to permit of transportation from place to place; furthermore, the measuring-tube is jacketed with water to prevent changes of temperature affecting the gas-volume. The apparatus consists essentially of the leveling-bottle A, the burette B, the pipettes P', P'', P''', and the connecting tube T. To set up the apparatus, the bottle A and burette B are connected by the long piece of $\frac{1}{4}$ -in. rubber tubing; similarly B and the pipettes P', P'', P''' are connected with the connecting tube T by rubber connectors carrying pinch-cocks; lastly, the

¹ J. M. Morehead, 143 Lake Street, Chicago, has devised an apparatus, a description of which is just at hand, which would seem to have many good points.

rubber connector and pinch-cock d are placed in position upon the end of T. The water-jacket is filled, preferably with distilled water, and about 150 cc. of water put into the bottle. Pipette P' is filled about half-full of potassium hydrate by removing the stoppers carrying the bent tube and rubber bag; all the



FIG. 26. — Orsat's Gas Apparatus

pinch-cocks but d being closed, the bottle A is raised and the burette filled with water nearly to the connector; d is closed, and e, the pinch-cock upon P', opened, the bottle lowered, thus sucking the reagent up into the front limb of P' and nearly to the capillary; sufficient reagent is poured into the rear limb of P' to leave about a half-inch of liquid standing in it when the reagent is in its capillary stem.

Manipulation. The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette and the rubber connector. This is effected by opening wide the pinch-cock upon the connector, the bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 cc., so that an error of a half-inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening dand raising the leveling-bottle. The apparatus is now ready to receive a sample of gas (or, for practice, air). The burette, after being filled, is allowed to drain one minute by the sand-glass, c is snapped upon its rubber tube, and the bottle A raised to the top of the apparatus. By gradually opening c, the water is allowed to run into the burette until the lower meniscus stands upon the 100 or the o mark (according to the graduation of the apparatus). The gas taken is thus compressed into the space occupied by 100 cc., and, by opening d, the excess escapes. Open c, bring the level of the water in the bottle to the same level as the water in the burette, and take the reading, which should be 100 cc. Special attention is called to this method of reading: if the bottle be raised, the gas is compressed; if lowered, it is expanded.

Determination of Carbon Dioxide. The gas to be analyzed is invariably passed first into the pipette P', containing the potassium hydrate for the absorption of carbon dioxide ("carbonic acid"), by opening e and raising A. The gas displaces the reagent in the front part of the pipette, laying bare the tubes contained in it, which, being covered with the reagent, present to the gas a large absorptive surface; the reagent moves into the rear arm of the pipette, displacing the air over it into the flexible rubber bag, which prevents its diffusion into the air. The gas is forced in and out of the pipette by raising and lowering A, the reagent is finally brought approximately to its initial point on the stem of the pipette, the burette allowed to drain one minute, and the reading taken. The difference between this and the initial reading represents the cubic centimeters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed the second time into P' and the reading taken as before. These two readings should agree within 0.1 per cent.

Determination of Oxygen. The residue from the absorption of carbon dioxide is passed into the second pipette, P", containing an alkaline solution of potassium pyrogallate, until no further absorption will take place. The difference between the reading obtained and that after the absorption of carbon dioxide represents the number of cubic centimeters of oxygen present.

Determination of Carbonic Oxide. The residue from the absorption of oxygen is passed into the

third pipette, *P*^{"''}, containing cuprous chloride, until no further absorption takes place; that is, in this case, until readings agreeing *exactly* (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen represents the number of cubic centimeters of carbonic oxide present.

Determination of Hydrocarbons. The residue left after all absorptions have been made may consist in addition to nitrogen, the principal constituent, of hydrocarbons and hydrogen. Their determination is difficult for the inexperienced. If desired, a sample of the flue-gas should be taken, leaving as little water in the apparatus as possible, and sent to a competent chemist for analysis.

Accuracy; Time Required. The apparatus gives results accurate to 0.2 of 1 per cent.

About twenty minutes are required for an analysis; but using two apparatus, two analyses may be made in twenty-five minutes.

Notes. The above-described method of adjusting the reagents is the only one that has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinch-cock c upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 cc. of gas is exactly analogous to filling a measure heaping full of grain and striking off the excess with a straight-edge: it saves arithmetical work, as cubic centimeters read off represent percentage directly. It often happens when e is opened, c being closed, that the reagent in P' drops. This is due not to a leak as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in P'' and P''' absorbing oxygen with great avidity; hence, if freely exposed to the air, they would soon become useless.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage present is so small, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given: if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon dioxide; similarly, if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but oxygen as well.

The use of pinch-cocks and rubber tubes, original with the author, although recommended by Naef, is considered by Fischer to be inaccurate. The experience of the author during fifteen years, however, does not support this assertion, as they have been found to be fully as accurate as glass stop-cocks, and very much less troublesome and expensive.

In case any potassium hydrate or pyrogallate be sucked over into the tube T, or water in A, the analysis is not spoiled, but may be proceeded with by connecting on water at d, opening this cock, and allowing the water to wash out the tubes thoroughly. The addition of a little hydrochloric acid to the water in the

bottle A will neutralize the hydrate or pyrogallate, and the washing may be postponed until convenient.

After each analysis the number of cubic centimeters of oxygen and carbonic oxide should be set down upon the ground-glass slip S provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity (see "Reagents") of each reagent, the condition of the apparatus can be ascertained at any time, and the reagent can be removed in season to prevent incorrect analyses.

Reagents. — The reagents used with the foregoing apparatus are prepared as follows:

Hydrochloric Acid (Sp. gr. 1.10). Dilute "muriatic acid" with an equal volume of water. In addition to its use for preparing cuprous chloride, it is employed in neutralizing the caustic solutions which are unavoidably more or less spilled during their use.

Acid Cuprous Chloride. The directions given in the various text-books being troublesome to execute, the following method, which is simpler, has been found to give equally good results. Cover the bottom of a quart bottle with a layer of copper oxide or "scale" $\frac{3}{8}$ in. deep; place in the bottle a number of pieces of rather stout copper wire reaching from top to bottom, sufficient to make a bundle one inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp. gr. Shake the bottle occasionally, and when the solution is colorless, or nearly so, pour it into a smaller bottle for filling the gas pipette containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp. gr.). By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

The absorption capacity of the reagent, according to the author's experience with Orsat's apparatus, is its own volume of carbon monoxide.

Care should be taken that the copper wire does not become entirely dissolved, and that it extends from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to exclude the air, which turns the solution brown and weakens it.

Potassium Hydrate. (a) For carbon dioxide determination 500 grams of the commercial hydrate are dissolved in 1 liter (quart) of water. Absorption capacity: 1 cc. absorbs 40 cc. CO_2 .

(b) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydrate are dissolved in 100 cc. of water.

Potassium Pyrogallate. The most convenient method of preparation is to weigh out 5 grams of the solid acid upon a paper, pour it into a funnel inserted in the gas pipette and pour upon it 100 cc. of potassium hydrate (a) or (b). The acid dissolves at once, and the solution is ready for use. If the percentage of oxygen in the mixture does not exceed 28, solution (a) may be used; if this amount be exceeded, (b) must be employed. Otherwise carbonic oxide may be given off even to the extent of 6 per cent. Absorption capacity: 1 cc. absorbs 2 cc. oxygen.

Attention is called to the fact that the use of potas-

sium hydrate purified by alcohol has given rise to erroneous results.

CALCULATIONS

The object in analyzing the chimney gases is to furnish additional data for the engineer besides those usually given by the evaporative test of the boiler. In fact, before incurring the trouble and expense of this latter test, the boiler plant should be tuned up by, so to speak, or submitted to, a preliminary test or series of tests with a gas apparatus and a flue thermometer; the proper adjustment of dampers should be made, and leaks stopped in the setting.

An example will make this clear. The plant to be tested was one employing forced draft; and, as the gas analysis showed a large excess of air, the blower engine was slowed down and the results shown below in column I were obtained. A large excess of air still being shown, the engine was slowed down more, giving the results shown in column 2; and even more than this, as shown in column 3.

	1 ¹	2	3
Heat going into water	59.6	67.8	70.0
Heat going into gases	33.2	23.6	17.8
Heat lost (unaccounted for)	7.2	8.6	12.2
Evaporation lb. water from and at 212 deg.	9.8	II.2	11.0
Excess of air per cent2	25.0	130.0	55.0

¹ Other data of interest in connection with this test are the following:

Duration of test 14 hours; 4 horizontal return-tubular boilers.
Area of grate 48×78 inches = 104 sq. ft. (4 boilers)
Area of water-heating surface $= 6328$ sq. ft.
Ratio
Air per pound coal

This evaporative test shows simply the percentage of heat absorbed by the water, and gives no idea of what becomes of the remainder. The composition and temperature of the gases tell us what part of the heat is passing up chimney; the analysis of the ash, what is the loss due to unconsumed coal: the chemical examination gives, then, these further data: (1) loss in chimney gases; (2) loss due to formation of carbonic oxide; and (3) loss due to carbon in ash; leaving as unaccounted for only the loss due to radiation and conduction.

The calculations involve the determination of the number of pounds of air per pound of coal, and the volume of gas passing up chimney with its temperature; we must know furthermore the heating value, or calorific power, of the coal.

(1 *a*) Pounds of Air Per Pounds of Coal. — The analysis of a chimney gas gave: carbonic acid 11.5, oxygen 7.4, carbonic oxide 0.9, nitrogen 80.2 per cent. The number of cubic feet of each of these gases in 100 cubic feet of chimney gas would then be represented by these figures, since the gas analysis is given in percentage, or parts by volume. The weight of each of these gases is found by multiplying the number of cubic feet by the weight of a cubic foot. For example, the

Loss of heat in ch	imney gases	
Coal burned per se	q. ft. per hour	
Water evaporated	from and at 212 deg. per sq. ft	
Quality of steam		0.9 80

Coal used, Pocahontas of the following analysis:

С	н	S	N and O	Water	Ash	Heating Value
81.9	4 · 5	I.0-	2.9	0.03	9.3	14.530 B.t.u.

weight of a cubic foot of carbonic acid is 0.1234 lb.; 11.5 cu. ft. therefore weigh 1.419 lb. The weights and volumes of each of the gases are shown below:

	Cu. ft. in 100 cu.	Weight of one	Weight of gas in
	ft. chimney gas	cu. ft. gas in lb.	100 cu. ft. in lb.
CO ₂	11.5	0.1234	1.419
со	0.9	0.0781	0.070
0	$7 \cdot 4$	0.0893	0.661

Carbonic acid is $\frac{32}{44}$ oxygen; that is,

 $\frac{O_2}{CO_2} \quad \frac{2 \times I6}{I2 + (2 \times I6)} = \frac{32}{44} = \frac{8}{II} \text{ O and } \frac{3}{II} \text{ C}$

In 1.419 lb. carbonic acid there are, then, $\frac{8}{11} \times$ 1.419 or 1.033 lb. oxygen and 0.386 lb. carbon.

Similarly, carbonic oxide is $\frac{16}{28}$ oxygen; that is,

 $\frac{O}{CO} \frac{I6}{I2 + I6} = \frac{I6}{28} = \frac{4}{7} O \text{ and } \frac{3}{7} C$

In 0.0703 lb. carbonic oxide there are consequently 0.0402 lb. oxygen and 0.0301 lb. carbon.

In 100 cubic feet of chimney gas there are:

That is, for every 0.416 lb. carbon there are 1.734 lb. oxygen, or 4.168 pounds of oxygen per pound of carbon. Air is 23.1 parts by weight oxygen; that is, in 100 pounds of air there are 23.1 pounds of oxygen: 4.168 pounds of oxygen represent 18.04 pounds of air. There are therefore in the chimney gas under consideration 18.04 pounds of air per pound of carbon.¹ The coal used was, however, but 83 per cent. carbon; consequently, this figure must be diminished accordingly, giving 14.97 pounds of air per pound of coal reckoned from the carbon. The oxygen in the coal combines with one-eighth of its weight of hydrogen, and the remaining hydrogen requires 36 pounds of air per pound for combustion; so that

$$36\left(\circ.\circ25b - \frac{\circ.\circ04}{8}\right) = \circ.88 \text{ pounds}$$

of air to combine with the hydrogen.

14.97 + 0.88 = 15.85 pounds of air per pound of coal.

The previous calculation is accurate but tedious. For rapid technical work the following may be used: The ratio of air actually used to that theoretically necessary may be expressed by the formula

$$\frac{21}{21 - \frac{79}{N}}$$

in which O and N represent the percentages of oxygen and nitrogen respectively in the flue gas as found by analysis. Applying it in this case we have

$$\frac{\frac{2I}{2I - \frac{79 \times 7.4}{80.2}} = \frac{\frac{2I}{13.7}}{13.7} = \frac{1.533 \text{ ratio}}{1.533 \text{ ratio}}$$

Multiplying this by 11.54, the theoretical number of pounds of air per pound of carbon, we obtain 17.69 as against 18.04 above.

¹ Theory requires 11.54 lb.

(1 b) Percentage of Heat Lost in Chimney Gases. — We need to know here the composition and temperature of the gases, their specific heat, the chemical analysis and the heating value of the coal. The analysis of the gases has just been given; and we calculate from this what volume of gases of this composition would be formed from the combustion of one pound of coal. Knowing their rise of temperature and specific heat, we can calculate the quantity of heat they carry off; and, dividing this by the heating value of the coal, we obtain the percentage of heat passing up chimney.

The composition of the gases is the same as given under 1a, "Pounds of air per pound of coal." The chemical analysis of the coal is: moisture 1.5 per cent., sulphur 1.2, carbon 83.0, hydrogen 2.5, ash 11.4, oxygen and nitrogen (by difference), 0.4. In one pound of coal there are 0.83 lb. carbon; of this suppose but 0.80 lb. to be burned, the remaining 0.03 lb. going into the ash. As both carbonic acid and carbonic oxide were formed, we must calculate what part of the o.80 lb. carbon produced each. From the preceding calculation we found that the amount of carbon in these two gases was 0.416 lb., made up of 0.386 lb. coming from the carbonic acid, and 0.030 lb. from the carbonic oxide: that is, $\frac{386}{416}$ produced carbonic acid, and $\frac{30}{416}$ produced carbonic oxide. Of the 0.80 lb. carbon, $\frac{386}{416}$, or 0.742 lb., produced carbonic acid, and 0.058 lb. produced carbonic oxide. We must next determine how much carbonic acid is produced from 0.742 lb. carbon. From the calculation 1a, of the pounds of air per pound of coal, we see that

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in 11.5 cubic feet of carbonic acid there are 0.386 lb. carbon; or we may say that 0.386 lb. carbon produces 11.5 cu. ft. carbonic acid, and consequently 0.742 lb. would produce 22.1 cu. ft.

386:742::11.5:x. x = 22.1

Similarly we see that 0.03 lb. carbon produced 0.9 cu. ft. carbonic oxide; 0.058 lb. carbon therefore produces 1.74 cu. ft. carbonic oxide.

To obtain the volume of oxygen, we can make the proportion

per cent. carbonic acid : per cent. oxygen :: cubic feet of carbonic acid : cubic feet of oxygen

or

$$11.5:7.4:22.1:y$$
. $y = 14.2$ cubic feet.

In the same way we can determine the volume of the nitrogen.

11.5:80.2:22.1:z. z = 154.1 cubic feet nitrogen.

One pound of coal burned to form a chimney gas of the volumetric composition given in the gas analysis yields as follows:

> 22.10 cubic feet carbonic acid 1.74 cubic feet carbonic oxide 14.20 cubic feet oxygen 154.10 cubic feet nitrogen 192.14 cubic feet chimney gases¹.

¹ The sum total of these figures for the volume of the chimney gas is 192.14 cu. ft., which is surprisingly close to the figure (193.7 cu. ft.) obtained by calculating the amount of air required, from the chemical composition of the coal, and taking into consideration the excess of air, 53.3 per cent. as found by the formula under the title "Pounds of air per pound of coal," already explained.

The temperature of the escaping gases was 527 deg. F.; that of the air entering the grate, 77 deg. F., a rise of temperature of 450 deg. F.: the specific heats (see page 29) and weights of a cubic foot of these gases are as follows:

S	p. ht. 🛛 🔪	Weight cu. ft.
Carbonic acid	0.227	0.1234 lb.
Carbonic oxide	0.245	0.0781
Oxygen	0.217	0.0893
Nitrogen	. 244	0.0784
Water vapor	.480	0.0500

The heat carried off by each gas is its weight (= volume \times weight of cubic foot) \times rise of temperature \times specific heat; that is, for

	Vol.	Weight	Rise	Sp. ht.	B.t.u.
Carbonic acid	.22.1	× 0.1234	X 450 X	(0.227 =	278.6
Carbonic oxide	.1.74	× 0.0781	X 450 X	(0.245 =	15.0
Oxygen	14.2	X 0.0893	\times 450 >	< 0.217 =	123.9
Nitrogen	. 154.1	× 0.0784	\times 450 \times	(0.244 ==	1326.6
					1744.1

Besides these gases there is another, passing up chimney and carrying off heat, of which we have taken no cognizance, namely, water vapor or steam: it comes from the moisture in the coal, from the moisture in the air which burns the coal, and from the moisture formed by the burning of the hydrogen contained in the coal.

The moisture in the coal shown by the analysis is 1.5 per cent. = 0.015 lb.; the hydrogen in the coal is 2.5 per cent., which, when burned, gives nine times its weight of water = $0.025 \times 9 = 0.225$ lb. The moistture in the air is 0.00085 lb. per cubic foot at 60 deg. F., if it be saturated; it was, however, only half-saturated, = 0.000425 lb. There were required 18 pounds of air per pound of coal (as shown in the calculation above, under "pounds of air per pound of coal") or 223 cu. ft. 223 × 0.000425 = 0.095 lb. moisture in the air. Total moisture = 0.015 + 0.225 + 0.095 = 0.335 lb. The heat carried off is 0.335 × 450 × 0.480 = 72.3 B.t.u., and the total heat carried off is 1744.1 + 72.3 = 1816.4 B.t.u. Heating value of the coal by the Mahler bomb is 13,000 B.t.u. and the percentage lost in gases is $\frac{1816.4}{13,000}$ = 14.0 per cent.

The foregoing calculation is longer and even more tiresome than the former, which involved the calculation of the pounds of air per pound of coal. A number of methods have been proposed which give results approximating this and which are sufficiently accurate for technical work. The formula

Loss in chimney gases =
$$(0.011 + \frac{100 - \% CO_2}{\% CO_2} 0.0605)t' - t$$

in which t' represents the temperature in the chimney and t that of the outside air, both in *Centigrade* degrees, gives close results and is independent of the composition of the coal: applied to the problem in question the loss comes 14.4 per cent., or 0.4 per cent. higher than by the other.

Bunte has devised the chart figured below (Fig. 27), which enables us to determine the loss by inspection. By noting the point at which the diagonal representing the percentage of carbonic acid (CO_2) cuts the horizontal line representing the actual temperature in degrees

Fahrenheit, and dropping a perpendicular from this down to the base-line, the percentage of heat lost is shown on the base-line. If the temperature be 510 deg. F. and the percentage of carbonic acid 11.5, we find that the loss is about 17 per cent., or 3 per cent. higher than given by other methods. This method gives results from 3 to 5 per cent. higher than the others.



FIG. 27. - Bunte's Chart

In general it may be said that the chimney gases from a well-stoked plant should contain at least 10 to 12, or better 13 to 15 per cent. of carbonic acid with practically no carbonic oxide.

Loss due to the formation of carbonic oxide. On page 89 we notice that 0.058 lb. of carbon burned to carbonic oxide: for every pound of carbon burned to carbonic oxide there is a loss of 10,190 B.t.u., in this case, a loss of $(10,190 \times 0.058)$ 591 B.t.u. The heating value of the coal is 13,000 B.t.u.; hence the loss is $\frac{591}{13,000}$ or 4.5 per cent.

Loss due to unconsumed carbon or coal in the ashes. The ashes are sampled as in the case of coal, grinding them in the iron mortar, and the percentage of moisture (if any) is determined. They are ignited after the manner of determining ash in coal, and the loss is figured as carbon. Knowing the total weight of ashes produced, the total weight of carbon in them can be figured, this calculated over into coal, which, divided by the weight of coal fired, gives the percentage of coal going through the fire unconsumed.

B. Examination of Chimney Gases by Automatic Apparatus

These depend for their action either upon the continuous weighing of a changing but definite volume of chimney gas, as in the "Econometer" of Arndt,¹ or upon the continuous weighing a globe in a changing atmosphere of the gas, as in the Gas Balance of Custodis, or upon the laws governing the flow of gases through small orifices, as in the Gas "Composimeter" of Uehling.

Arndt's Econometer.¹—This is shown in Fig. 28. It consists of a counterpoised vessel 18 through which the chimney gases are caused to circulate: the per-

¹ Arndt in Aachen, Germany, has devised another instrument something like Uehling's called the *ados*, "heating-effect-meter."
centages of carbonic acid contained in the gases are read off directly from the index on the scale 27 of the balance.

The chimney gases are drawn continuously by the draft in the chimney itself by aspirator 67 from the boiler flue 61 first through a gas filter 56, a cotton wool



FIG. 28. - Arndt's Econometer

filter 51 to remove ashes and soot, and a drying tube 45, then through $\frac{1}{4}$ -inch tubing and fittings 42, 23, 19, etc., into the vessel 18 and out through 22, 62, 65, etc., into the main flue.

The following table shows the loss of heat in boilers by the indications of the Arndt Econometer, using ordinary coal:

ENGINE-ROOM CHEMISTRY

PER CENT. CARBONIC ACID

2 3 4 5 6 7 8 9 10 11 12 13 14 15

VOLUME OF AIR MORE THAN THEORY

9.5 6.3 4.7 3.8 3.2 2.7 2.4 2.1 I.9 I.7 I.6 I.5 I.4 I.3 Theory = I.0

PER CENT. LOSS OF HEAT TEMP. OF CHIMNEY GASES 518 DEG. 90 60 45 36 30 26 23 20 18 16 15 14 13 12



FIG. 29. — Custodis Gas Balance

The Custodis Gas Balance. — This is shown in Fig. 29, and is practically the same as Arndt's instrument except that where the latter uses a balanced globe full of chimney gas, in a chamber of air, Custodis uses a balanced globe of air in a chamber of chimney gas.

In the figure k and l are the balanced globes, and f the chamber (at the right) into which the chimney gas is sucked through, just as in the previous case, the gas being filtered but not dried; the percentage of carbonic acid is read off on the scale n; a gentle current of air is caused to circulate through e, the chamber (at the left) in which the globe k hangs.

Uehling's Gas Composimeter is shown diagrammatically in Fig. 30 and as actually built in Fig. 31. As



FIG. 30. — Uehling's Gas Composimeter. Diagram

stated above, it is based on the laws governing the flow of gases through small apertures.

If two such apertures, A and B (Fig. 30) form respectively the inlet and outlet openings of chamber C and a uniform suction is maintained in the small chamber C' at the left by the aspirator D, the action will be as follows:

Gas will be drawn through the aperture B into the chamber C', creating suction in chamber C, which, in

turn, causes gas to flow through the aperture A. The velocity with which the gas enters through A depends



FIG. 31. - Uehling's Gas Composimeter

on the suction in the chamber C, and the velocity with which it flows out through B depends upon

the excess of the suction in chamber C' over that existing in chamber C; that is, the effective suction in C'. As the suction in C increases, the effective suction must decrease, and hence the velocity of the gas entering at A increases, while the velocity of the gas passing out through B decreases, until the same quantity of gas enters at A as passes out at B. As soon as this occurs no further change of suction takes place in the chamber C, providing the gas entering at A and passing out at B be maintained at the same temperature.

If, from the constant stream of gas while flowing through chamber C, one of its constituents is continuously removed by absorption, a reduction of volume will take place in chamber C and cause an increase in suction and consequently a decrease in the effective suction in C'. Hence the velocity of the gas through A will increase and the velocity through B will decrease until the same quantity of gas enters at A as is absorbed by the reagent, plus that which passes out at aperture B.

Thus every change in the volume of the constituents we are absorbing from the gas causes a corresponding change of suction in the chamber C.

If the manometer tubes p and q (Fig. 30) communicate respectively with the chambers C and C', the column in the tube q indicates the constant suction in C, and the column in tube p indicates the suction in C', which suction is a true measure of the percentage of the constituent we wish to measure in the gas.

PRACTICAL APPLICATION OF THE PRINCIPLE OF THE GAS COMPOSIMETER

To embody the principles described in a practical apparatus, the following conditions must be fulfilled:

a. The gas must be brought to the instrument under a constant tension and must be drawn through the apertures with a continuous and perfectly uniform suction.

b. Both apertures must be located in a medium of constant temperature.

c. Provision must be made that the apertures remain perfectly clean.

d. The chamber C must be made perfectly tight so that no gas can enter except through the aperture A.

e. Provision must be made to render the gas free from moisture.

f. The constituent to be measured must be completely absorbed after the gas passes through A and before it passes out at B.

Fig. 31 shows the apparatus as actually constructed. C is the regulator insuring a constant suction. O is that portion of the apparatus which contains apertures A and B (Fig. 30), and which is kept at the constant temperature of steam at atmospheric pressure. E and E' are saturators through which the gas passes, respectively, before entering A and before entering B, thus insuring the same quantity of moisture in the gas at both A and B. F contains the absorbent and is situated between the two apertures. S is the scale from which the percentage of CO_2 can be read at will, while

G is the gage which makes a continuous record of the same. M is the reservoir which supplies F with the absorbent, while N is the receiver for this solution after it has been used.

In general these apparatus are difficult to adjust and to keep in adjustment, requiring checking by the gas analytical apparatus; yet it is said that the Uehling Gas Composimeter has recently been developed into a very practical instrument, which can be used continuously and which needs very little attention. Their indications are within about 0.5 per cent. of those given by the chemical apparatus. Only the presence of carbonic acid is indicated by them.

V

BOILER SCALE - PITTING AND CORROSION

THE troubles indicated in the title of this chapter spring mainly from one source, impure or "hard" water, although very pure and soft water may also cause corrosion.

Hard water may be defined as water containing in solution mineral compounds that curdle or precipitate soap. Under this definition are included the saline waters, as sea-water and some of the alkali waters of the West, as well as those usually called "hard." The substances which render water hard are salts of lime, magnesia, and iron, which are held in solution ¹ in cold water and precipitated on boiling. These salts are usually either carbonates or sulphates, and are precipitated for different reasons: the carbonates are held in solution by the carbonic acid which the water absorbs in falling through the atmosphere and passing through the earth. Water containing carbonic acid dissolves the carbonates of the bases named, so that

¹ Care should be taken to note the distinction between "solution" and "suspension" as defined on p. 2, footnote. Solution is exemplified by the mixing of water and salt so that the latter disappears or dissolves and cannot be separated by filtering through paper. Suspension is shown in the mingling of water and clay, the latter separating from the water on standing a sufficient length of time. they exist there really as bicarbonates. On the removal of the carbonic acid, either by chemical agents or by boiling, the carbonates are precipitated. "Sulphate of lime" or calcium sulphate is, contrary to the usual experience, more insoluble in hot water than in cold; consequently when water containing it is heated, it is thrown down, and completely so, at a pressure of 35 pounds.

Magnesium compounds, except the carbonate, are soluble, and are usually not precipitated; the statement, however, is made that magnesium sulphate forms scale in the presence of calcium carbonate. Magnesium chloride is decomposed at temperatures a little above the boiling-point of water into hydrochloric acid and magnesia. The hydrochloric acid dissolves any scale, converting it into calcium chloride. The magnesia, coming in contact with any soda ash used in softening the water, changes it over to caustic soda, which combines with any carbonic acid that happens to be present.

Magnesium chloride + hydrogen oxide = hydrogen chloride + magnesium oxide (water) (hydrochloric acid) (magnesia) MgO MgCl₂ + H_2O 2HCl + Calcium carbonate +hydrogen chloride=calcium chloride +hydrogen carbonate Chalky boiler scale (muriatic acid) (carbonic acid+water) CaCO₃ CaCl₂ $+H_2CO_3$ +2HCl ----- $(=H_2O+CO_2)$

ENGINE-ROOM CHEMISTRY

Magnesium oxide + sodium carbonate = sodium oxide

+magnesium carbonate

(Magnesia) MgO	(soda ash) + Na_2CO_3	= Na ₂ O $+$ MgCO ₃
Sodium oxide Na ₂ O	+water + H ₂ O	= sodium hydrate = 2NaOH
Sodium hydrate	+carbonic acid	=sodium carbonate
2NaOH	$+ CO_2$	= Na ₂ CO ₃ $+$ H ₂ O

Hardness, due to the bicarbonates, which is lessened by boiling, is said to be "temporary," while that which is not removed in this way is said to be "permanent."

Low hardness, to 200 parts of calcium carbonate per million, is usually determined by means of a standard solution of soap. To this end 50 cubic centimeters of the water are measured into a tall 200-cc. clear-glass bottle; alcoholic soap solution is added to it from a burette, shaking well after each addition, until a lather is obtained which covers the entire surface of the liquid, with the bottle lying on its side, and is permanent for five minutes. From the number of cubic centimeters of soap solution used the hardness of the water may be calculated by the use of Clark's table below: it is usually reported in this country ¹ in parts of calcium carbonate (CaCO₃) per million.

¹ Also in France. In England a degree of hardness means one grain of calcium carbonate per imperial gallon; in Germany, one part of calcium oxide (CaO) per hundred thousand. To convert grains per gallon to parts per million multiply by 17.18.

PITTING AND CORROSION

Cc. soap sol.	Pts. CaCO ₃ per million	Cc. soap	Pts. CaCO ₃	Cc. soap	Pts. CaCO ₃
0.7 1.0 2.0 3.0 4.0 5.0	0.0 5.0 19.0 32.0 46.0 60.0	6.0 7.0 8.0 9.0 10.0 11.0	74.0 89.0 103.0 118.0 133.0 148.0	12.0 13.0 14.0 15.0	164.0 180.0 196.0 212.0

CLARK'S TABLE OF HARDNESS

If, for example, 8 cc. soap solution were required, it signifies that the mineral compounds in the water produce a degree of hardness in the water equivalent to that which would be produced by 103 parts of calcium carbonate ($CaCO_3$, chalk) in one million parts of water.

For waters which are harder than 200 parts per million, a solution of soap ten times as strong may be used, the end point being taken at the time when sufficient soap has been added to deaden the harsh sound produced on shaking the bottle containing the water.¹

The standard soap solution can be obtained from dealers in fine chemicals and apparatus, or from an analytical chemist. (The other methods of determining hardness, "temporary" by means of hydrochloric acid (Hehner's method), "permanent," by sodium carbonate and hydrate (Pfeifer and Wartha's method), and magnesia by lime-water (Pfeifer's method), require the services of a skilled chemist.)

¹ See paper by C. R. Walker in Tech. Quarterly, xvii, 281.

This determination of hardness by soap test enables us to estimate what quantity of soda crystals to use in softening the water; but without a chemical analysis it is impossible to calculate *exactly* how much will be required, since we do not know how much calcium sulphate (CaSO₄) there may be, or whether magnesium salts are present. In any event the water will probably be left slightly hard.

If the soap test indicates there are 103 pounds of calcium carbonate in one million pounds of water, as in the example just cited, the estimate of the quantity of soda crystals required is made by means of the formula,

soda crystals : calcium carbonate :: weight soda crystals : weight calcium carbonate,

or, chemically expressed,

(Na₂CO₃ + 10H₂O): CaCO₃ :: x : 103 soda crystals : calcium carbonate

 $2 \times 23 + 12 + (3 \times 16) + 10 \times (2 + 16) : 40 + 12 + 48 :: x : 103$ 286 100 :: x : 103

whence x = 294 lb. soda crystals per million pounds water, or 120,000 gallons, = 2.45 lb. per thousand gallons.

If the calculation be desired where soda ash, or dry soda crystals, is to be used, it is as follows:

Na₂CO₃ = $(2 \times 23) + 12 + (3 \times 16) = 106 : 286 :: y : 2.45$ y = 0.91 lb. soda ash per 1000 gallons.

Expressing this in the form of a rule it reads thus: To determine the number of pounds of soda crystals required per thousand gallons of water, multiply the

hardness expressed in parts of calcium carbonate per million by the factor 0.0238: the quantity of soda ash is found by multiplying by the factor 0.00883. While the amount thus obtained by calculation is theoretically correct, experience shows that it is excessive, and that only about one-quarter of this quantity is actually needed.

Effects of Hard Water.—The effects of hard water are:

1. The production of scale with its accompanying losses.

2. The corrosion of the boiler shell.

3. The causing of foaming in the boilers.

1. The production of scale causes (a) Waste of fuel; (b) Expense in removing; (c) Burning out of crown sheets and corrosion of the boiler shell.

(a) Waste of fuel. Scale being a poorer conductor of heat than iron, it retards the transference of heat from the metal to the water: the approximate loss is as follows:

Thickness of scale	Loss of heat
in inches	per cent.
$\frac{1}{16}$	13–16
1	38–50
12	60-150

This means that the scale one-sixteenth of an inch thick causes a loss of heat of about 16 per cent., or one-seventh of the coal fired. Scale, however, is not always a detriment. In some cases it serves to prevent general corrosion. In using a very pure natural water containing much carbonic acid, as Loch Katrine water, it is recommended to cover the inside of the boiler with a scale 1–50 in. thick. With marine boilers, a mixture of milk of magnesia and gypsum is added to the feed-water for this same purpose.

(b) Removal of scale. Boiler scale is of two varieties: (1) a hard, crystalline, adherent scale which is due to the presence of calcium sulphate: originally precipitated as a powder, it is changed over into the crystalline form by heat. This serves as a binding material for any precipitate in the water, as calcium or magnesium carbonate, iron rust, clay, mud, or sand. (2) A soft, powdery, scale due to the precipitated carbonates and the materials just mentioned. The soft scale may be removed by blowing off the boiler, first using the scum cocks, and washing out the powder with a hose stream. For removing adherent scale, kerosene has given good results in some cases: the oil floats on the surface of the water, penetrates the scale as the boiler is blown off, and upon firing up again the expansion of the kerosene vapor causes the scale to crack off from the places to which it adheres and enables it to be removed by blowing off. The use of various acids - hydrochloric, acetic, or even tannic - is not to be recommended, as they attack not only the scale, but also the boiler itself. A hard, firmly adherent scale can only be removed by a hammer and chisel.

(c) Burning out of the crown sheets and corrosion of the boiler shell. To transmit the same quantity of heat, a crown sheet covered with scale has to be heated to a higher temperature than a clean one, causing a burning or oxidation of the iron. To a similar cause is due the corrosion or pitting upon the inside of these sheets. Particles of cylinder oil floating on the top of the water in the boiler become loaded with scum, sink to the bottom and adhere to it, acting like scale and preventing the transmission of heat. The sheet beneath them gets sufficiently hot to char and decompose the oil, loosening it and allowing the water to come in contact with the red-hot iron; this gives rise to a sudden evolution of steam and may cause an explosion, and in any case attacks the plate, forming a rust on the inside of the boiler shell.

> Iron + hydrogen oxide = iron oxide + hydrogen(water) $3Fe + 4H_2O = Fe_3O_4 + 4H_2$

2. The corrosion of the boiler shell. This has already been partly treated of in the foregoing paragraph. Corrosion is also due to organic matters or acids contained in natural waters, particularly those from swampy districts: these may contain tannic, humic, and carbonic acids which dissolve iron. Waters from mining districts are apt to contain mineral acids, particularly sulphuric from the oxidation of pyrites or other sulphur-containing ores. Polluted water containing salt, chlorides of calcium or magnesium and nitrates are also strongly corrosive. These produce general corrosion—a weakening of the shell. Fig. 32 from Peabody and Miller, "Steam Boilers," illustrates this well; it shows the protection of the plate by the rivet head.

Corrosion of steam pipes, particularly "returns," seems to be due mainly to carbonic acid and oxygen contained in the water, a small amount of carbonic acid dissolving an unlimited quantity of iron,¹ the process being a cyclic one. The carbonic acid driven off from the water in the boiler, goes with the water vapor and steam to the cooler part of the system, where it dissolves in the condensed steam and attacks the iron pipes with which it comes in contact.

Iron + carbonic acid = bicarbonate of iron + hydrogen²

 $Fe + 2H_2CO_3 = FeH_2(CO_3)_2 + H_2$ This bicarbonate of iron when it meets the heated part

of the return pipes or gets into the boiler itself is de-



FIG. 32. — General Corrosion

composed, giving oxide of iron or iron, rust and setting free the carbonic acid which promptly renews the attack.

Bicarbonate of iron = ferrous oxide + water + carbonic acid $FeH_2(CO_3)_2 = FeO + H_2O + 2CO_2$ Ferrous oxide + oxygen = ferric oxide $2FeO + O = Fe_2O_3$

As indicative of the effect of water containing carbonic

¹ This has been shown by Whitney, in *Journal American Chemical Society*, xxv (1903), 394.

² The gas often found in hot-water radiators is mainly hydrogen.

acid upon iron, the case may be cited of the corrosion of a stay within a boiler, produced by the discharge upon it of the cold feed-water containing carbonic acid.

The remedy for this carbonic acid corrosion consists in adding caustic soda, or, better, lime-water, to the feed-water. The quantity can be calculated as follows: water at ordinary temperatures dissolves its own volume of carbonic acid; that is, every gallon of water carries in 231 cubic inches of carbonic acid. One cubic inch of carbonic acid weighs 11.55 grains; the equation representing the reaction between caustic soda and carbonic acid is

sodium hydrate + carbonic acid = sodium carbonate + water 2NaOH + CO_2 = Na_2CO_3 + H_2O 2(23 + 16 + 1):(12 + 32)::x:11.55. x = 20.9 grains 80 : 44

of caustic soda per gallon, or three pounds to the thousand gallons. To determine the amount of slaked lime we can make the proportion

```
lime : caustic soda :: y : 3
CaO<sub>2</sub>H<sub>2</sub> : 2NaOH
74 : 80 y = 2.8 pounds.
2.8 pounds of slaked lime per thousand gallons.
```

Pitting, the term applied to local corrosion, may be formed by oil drops, as above indicated, or by the introduction of iron scale (forge scale), coke, chips of brass or copper into the boiler: these are all electronegative to the iron, cause a galvanic action between themselves and the iron of the boiler, with the usual result that the positive metal is dissolved — in this case the iron. Pitting may also be due to the fact that the boiler plates are not homogeneous. Fig. 33, also from Peabody and Miller, shows pitting at the corner of a flanged plate.

This pitting may be prevented by the introduction into the boiler of plates of zinc, a metal more positive than iron, which is dissolved in its place; this is frequently done with marine boilers.

It is not sufficient to hang zinc slabs in the boiler, or throw them in. They must be bolted on to projections from the boiler itself, making good electrical con-



FIG. 33. - Pitting of Iron

tact. For new boilers allow one square foot of zinc to each 50 feet of heating surface, and later half this amount.

Another source of pitting or corrosion of boilers, formerly of more frequent occurrence than at the present time, is the presence of animal or vegetable oils coming from cylinder lubrication. These were formerly used in a pure condition for this purpose: now cylinder oil does not usually contain more than 5 or 7 per cent. of these oils, the remainder being mineral oil. This small quantity is probably without appreciable

action upon the boiler. Whenever animal or vegetable oils are heated together with steam at high pressure, they are decomposed with the formation of glycerin and fatty acids—stearic, palmitic, oleic, and others. These acids at the high temperature attack the metals with which they come in contact. They are also one of the causes of the pitting of cylinders.

Glyceryl stearate + water = glyceryl hydrate + stearic acid tallow glycerin

Besides the causes of corrosion already considered, namely, (a) the high temperatures of the crown sheets, (b) the presence of bodies electronegative to the iron, as forge scale, cinders or coke, copper or brass chips, (c) animal oils, (d) acids, acetic, tannic, humic, sulphurous or sulphuric, and (e) polluted or sea-water containing nitrates and chlorides, the following corroding agencies may be noticed: (f) alkaline substances, as caustic soda and lime-water. These have little action upon iron but attack copper or brass fittings vigorously. (g) Strains upon iron. If iron be under strain this has a tendency to open the pores of the metal, admitting water and carbonic acid and increasing the oxidation of the iron. (b) The escape of a stream of water in a fine jet from a boiler seam may cause corrosion, from the continuous removal of the oxide of iron produced by the action of the water upon the iron.

3. The causing of foaming or priming in the boilers. This is most likely due to the precipitation of the scaleforming matter as a fine powder: these particles serve as points from which steam is liberated. This is a well-known fact and is taken advantage of by the chemist in boiling solutions which have a tendency to "bump," as the expression is; that is, they, after boiling for a time, suddenly become quiet for a few seconds, and with equal suddenness boil explosively over the entire surface, causing the liquid to run over. By the addition of a few pieces of ignited and quenched pumice-stone or bits of platinum-foil, the boiling proceeds regularly, currents of steam being seen to rise from them. This foaming can be shown by boiling a mixture of alcohol and water in a flask, when the boiling suddenly stops, and if the heating be continued the liquid becomes superheated: if the lamp be now removed and sand scattered into the flask it will almost empty itself by the violence of the boiling.

This foaming is seen less frequently with stationary boilers than with locomotives, for the reason that the feed-water is practically the same in the former case. In the latter case this trouble manifests itself in the West, where after using a hard water it is followed by that of the alkali belt: the alkali precipitates the lime and magnesia as carbonates from the hard water, in a finely divided condition, causing the foaming in the manner indicated above.

Remedies for Hard Water. — As to boiler compounds. J. M. Boon expresses the opinion that "The only compound to put into a boiler is pure water." It has been estimated that the actual cost, that is waste, of fuel, repairs, etc., due to hard water and boiler scale is about \$750 per year for each locomotive in the United States. While in the case of stationary boilers no such figures are available, it may be said in a general way that the life of the boiler would be increased threefold by the use of soft water, to say nothing of the gain accruing from continuous service.

Almost everything under the sun¹ has been proposed for the removal of boiler scale and softening of water, including potato parings, molasses, and tanbark. The last two act by virtue of the acids which they contain, the one acetic and the other tannic; these may act on the scale precipitated, but they corrode the shell of the boiler.

While the proper place for the treatment of water is outside the boiler, yet many prefer, on account of convenience, lack of room, or other causes, to soften the water in the boiler itself, and it is a question of the most suitable compound to employ. A proper substance is one that precipitates the salts which make water hard, in a powdery or flocculent condition so that they can be easily blown out. It should not be acid nor yield up acid on treatment. It should be cheap and easily applied. Salts of sodium (calcium or lime) fulfil all these conditions and are usually employed. Let us now see the action of some of the various compounds proposed.

Caustic soda or caustic lime (lime-water). These combine with the carbonic acid contained in the water in combination as bicarbonates, and, as this acid holds the calcium and magnesium carbonates in solution they are precipitated. Another action is to combine

¹ For a list of these, some 170 in all, see Davis, "Steam Boiler Incrustation and Corrosion," page 72.

with any acid — sulphuric from mines, carbonic from the air, tannic or humic acid from swampy waters.

Soda ash or sodium carbonate. This acts on the bicarbonates of lime or magnesia, forming bicarbonate of soda, which is decomposed by the temperatures in the boiler into carbonic acid and sodium carbonate. Unless magnesium chloride be present, decomposing as has been shown into the oxide, carbonate of soda has no power, unless in the cold, of fixing carbonic acid caustic soda or lime ("lime-water") is required for this. It transforms the sulphates into carbonates; changing what would be a hard, crystalline, adherent scale of gypsum into the powdery calcium carbonate which is easily blown out. The precipitation of these carbonates has a tendency to clarify the water if it contains clay or mud, not, however, to the extent to which a more flocculent precipitate does. It neutralizes acids, as does caustic soda, with, however, the liberation of carbonic acid. It is often used in connection with lime-water to soften hard water, its object being to precipitate the excess of lime used.

 $\begin{array}{rll} \mbox{Calcium bicarbonate} + \mbox{sodium carbonate} = \mbox{sodium bicarbonate} + \\ \mbox{CaH}_2(\mbox{CO}_3)_2 & + & \mbox{Na}_2\mbox{CO}_3 & = & \mbox{2Na}\mbox{HCO}_3 & + \\ \mbox{calcium carbonate} \\ \mbox{CaCO}_3 & \end{array}$

This on being boiled gives sodium carbonate and carbonic acid sodium bicarbonate = sodium carbonate + water + carbonic acid = Na₂CO₃ + H₂O +2NaHCO3 CO_2 calcium sulphate + sodium carbonate = calcium carbonate + $Na_2CO_3 =$ CaCO₃ CaSO₄ ++sodium sulphate Na₂SO₄ sulphuric acid + sodium carbonate = sodium sulphate + $Na_2CO_3 = Na_2SO_4$ H₂SO₄ + + carbonic acid + water

 $(\mathrm{H_2CO_3})\mathrm{CO_2} + \mathrm{H_2O}$

Sodium aluminate, made by fusing soda ash and alumina together, may, for practical purposes, be regarded as acting like caustic soda. In addition to the advantages enumerated for caustic soda, it has another, that aluminum hydrate is thrown down as a light, flocculent precipitate, which possesses to a marked degree the property of clarifying waters; hence it should carry down not only the carbonates of lime and magnesia, but organic matter, as humic acid, tannic acid, clay, mud and sand in such a condition that they could be easily removed by blowing off.

 $Sodium aluminate + calcium bicarbonate + water = \\ Na_2Al_2O_4 + CaH_2(CO_3)_2 + 2H_2O = \\ sodium carbonate + aluminum hydrate + calcium carbonate \\ Na_2CO_3 + 2AlO_3H_3 + CaCO_3$

Sodium fluoride. When sodium fluoride is added to water containing calcium bicarbonate, the water is rendered soft, calcium fluoride and sodium bicarbonate being formed.

 $\begin{array}{rll} \mbox{Calcium bicarbonate + sodium fluoride = sodium bicarbonate + } \\ \mbox{CaH}_2(\mbox{CO}_3)_2 & + & 2\mbox{NaF} & = & 2\mbox{NaHCO}_3 & + \\ & & \mbox{calcium fluoride (fluorspar)} \\ & & \mbox{CaF}_2 \end{array}$

A similar interchange takes place with calcium sulphate, or the corresponding magnesium compounds. Calcium fluoride is precipitated as a powder, and is about twice as soluble in water as calcium carbonate, one part dissolving, in about 26,000 parts of water, whereas 50,000 parts are required to dissolve the carbonate. Sodium fluoride is claimed not to attack valve metal nor iron, nor to cause foaming and to take up oil.

Trisodium phosphate. This is usually made by adding caustic soda to the ordinary phosphate of soda and is mildly alkaline in character. By its use, as has been noted, in the case of sodium aluminate, the waters are both softened and clarified. The lime and magnesia compounds are changed into phosphates which are insoluble, thus taken out of solution, and are flocculent, which drag down any substance in suspension as clay, mud, or precipitated calcium carbonate. In this condition the sludge is readily blown out.

The chemical action taking place is

Similar reactions take place with the bicarbonate and magnesium compounds.

Composition of Some Boiler Scales. - Boiler scales

naturally differ according to the waters from which they are formed; from fresh water they may or may not contain a quantity of calcium sulphate; from seawater it is the chief incrusting agent; while from brackish waters the scale contains large percentages of both. The reason for the absence of calcium carbonate in sea-water scale is found in the fact that the marine animals take out calcium carbonate for the material of their shells — oyster, mussel and barnacle shells, chalk and coral being mainly composed of it. Table III, from Lewes, shows the analyses of boiler incrustations from their different sources.

	River Water	Brackish Water	Sea-Water
Calcium carbonate	75.8	43.6	1.0
Calcium sulphate	3.7	34.8	85.5
Magnesium hydrate	2.6	4.3	3.4
Salt	0.4	0.6	2.8
Sand	7.7	7.5	1.1
Oxides iron and alumina	3.0	3.4	0.3
Organic matter	3.6	1.6	trace
Moisture	3.2	4.2	5.9
Totals	100.0	100.0	100.0

TABLE III

Table IV shows the composition of some boiler scales, together with the analyses of the waters from which they were formed.

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TABLE IV

CHEMICAL COMPOSITION OF SOME BOILER DEPOSITS TOGETHER WITH ANALYSIS OF THE FEED-WATERS

CONGRATION	Νο. τ		No. 2		No. 3		No. 4	
CONSTITUENTS	Scale	Water	Scale	Water	Scale	Water	Scale	Water
Essential Composition								
Calcium carbonate(CaCO ₃)	44.25		8.30		55.65		14.78	13.06
Anhydrite (CaSO ₄)			49.98		31.96			-
Calcium sulphate (2CaSO ₄ .H ₂ O)	50.75		29.73		—		74.07	19.2
Gypsum (CaSO ₄ .2H ₂ O)								
Magnesium hydrate	1.19		3.83		7.11			
Chemical Composition								
Lime (CaO)	44.38	45.0	36.43	4.60	44.32	15.5	38.80	15.23
Magnesia (MgO)	.82	8.5	2.64	-9	4.90	6.8	5.96	3.7
Ferric oxide and alumina	2.24		1.67		2.10		.08	0.1
Silica (SiO ₂)	•47		.88		trace		.65	
Water given off above 120								
deg.	3.68		3.04		2.31		İ.14	
Insoluble matter	.48		5.65		2.46			
Carbonic acid (CO ₂)	19.25		3.66		24.48		9.63	
Sulphuric anhydride (SO3)	28.22	21.9	45.21	4.0	18.76	8.9	43.65	12.3
Lime		22.5		trace		6.3		
Magnesia deposited on boil-								
ing		1.9		0.0		3.9		
Chlorine		29.3		-		9.1		

Water expressed in parts per 100,000. Scale expressed in per cent.

The following experiments will illustrate some of the points brought out in the preceding, regarding hard water and scale-formation.

Hard water. Prepare artificial hard water by dissolving calcium carbonate in water containing carbonic acid as follows: Lime-water is first made, then carbonic acid is passed into it; slake, with a small amount

of water, a piece of lime as big as a marble, putting the white, pasty mass into a quart bottle, nearly filling it with water, keeping it tightly corked, and shaking it from time to time. The clear liquid is lime-water. To save the trouble of its preparation a pint may be obtained from a druggist.

Make a generator for carbonic acid in the following manner: Procure a wide-mouthed bottle of about a half-pint capacity, fitted with a good cork, a thistle or funnel tube, a piece of $\frac{3}{16}$ -in. glass tubing a foot long, and a piece of rubber connecting tubing 2 inches long to pass over the glass tubing. By heating the glass tubing in the gas or alcohol-lamp, rotating it, to heat all sides equally, soften it, and make a right-angle bend with arm 2 inches long at each end of the tube, cut off one, making an elbow with 2-in. arms.

The tubing is cut by making a scratch upon it with a triangular file, then holding the tubing in the hands, with the thumb-nails together and opposite the scratch, the tube is partly pulled and partly bent apart, when it will break squarely at the scratch, leaving sharp edges. These should be removed by rotating the tubing against the file, otherwise they will cut the rubber connector or cork like a keen knife.

Now with a round file make two holes through the cork and fit the thistle tube into one and the elbow into the other, taking care that they make a snug fit. In fitting these tubes they should be wrapped with several thicknesses of towel and not held naked in the hand, as they make bad cuts in case of breakage: they may be wet or soaped to help their passage into the cork. By means of the rubber connector attach the two elbows together and cut off the longer one, or delivery tube as it is called, so that when the generator sets on the bench the delivery tube will be about oneeighth of an inch from it. When finished the generator will look like Fig. 34.



FIG. 34. —Carbonic Acid Generator

Six or eight bits of marble or limestone as large as marbles are put into the generator, and covered with water, a half-teaspoonful of strong muriatic acid being added from time to time; a brisk bubbling now takes place, and a gas, carbonic acid, is evolved from the

marble and conducted into half of the lime-water contained either in a beaker or bottle. A white precipitate of calcium carbonate takes place which, on continued passing of the gas, dissolves. It is not necessary to wait until it all dissolves, but after the gas has passed through the liquid for twenty minutes or half an hour, it may be discontinued, the liquid allowed to settle, and the clear solution used for the experiments. The chemistry of what has taken place so far is as follows:

Calcium carbonate + carbonic acid + water = calcium bicarbonate $CaCO_3$ + CO_2 + H_2O = $CaH_2(CO_3)_2$ (soluble)

(a) To show "temporary" hardness. Boil half a testtubeful of the "clear solution" and note that a white precipitate takes place, due to the fact that the carbonic acid is driven off which holds the calcium carbonate in solution; this white precipitate is calcium carbonate. This can be proved, if desired, by filtering off the precipitate, dissolving in hydrochloric acid note the bubbling due to carbonic acid — and treating the solution with ammonia and ammonium oxalate, when the characteristic white precipitate of calcium oxalate will appear. (b) To show the softening power of lime-water. Add lime-water to some of the "clear solution" in a testtube as long as a precipitate is produced. The precipitate is, as before, calcium carbonate, and is produced for two reasons: (1) because the lime-water combines with the carbonic acid, making calcium carbonate; and (2) because the carbonic acid which held some calcium carbonate in solution being removed, there is nothing to keep it in solution. Consequently it is precipitated. Lime-water is extensively used as a water-softening agent; caustic soda acts in an exactly similar manner. Keep some of the "softened" water to try its action with soap.

(c) To show the softening power of soda ash. Add a pinch of soda to some of the above-mentioned "clear solution," and note the familiar precipitate of calcium carbonate, due to the reason just given above.

To show the softening power of various "boiler compounds" (d) tri-sodium phosphate, (e) sodium fluoride, (f) sodium aluminate and others, obtain small samples from the dealers, dissolve in water, add to the "clear solution" and note the kind of precipitate formed. In all cases up to the present the precipitate has been calcium carbonate in a powdery shape, which is not as efficient for removing impurities from water as a flocculent or gelatinous form. In the case of the phosphate and aluminate, this kind of precipitate will be obtained.

(g) To show the effect on soap. Treat some of the "clear solution" in a test-tube with a solution of soap and note the curdy precipitate, lime soap, formed:

choose two test-tubes of practically the same diameter and put into one two inches in depth of the "clear solution" and into the other the same quantity of the "softened water." Add to each of these soap solution from a medicine dropper, noting the number of drops in each case until a permanent lather is produced. The "softened water" will require very much less soap to produce the same lather.

The equations below indicate what has taken place in the various experiments.

TEMPORARY HARDNESS

SOFTENING WITH LIME-WATER

SOFTENING WITH SODA ASH

Calcium bicarbo	onate + s	oda ash =	= calcium	carbonate	+	sodium	bi-
	(sodium	carbonat	te)			carbon	ate
$CaH_2(CO_3)_2$	2 + 1	$Na_2CO_3 =$	= Ca	LCO3	+	2NaHC	O_3

SOFTENING WITH TRISODIUM PHOSPHATE

 $\begin{array}{rl} \mbox{Calcium bicarbonate + trisodium phosphate = calcium phosphate +} \\ \mbox{}_{3}\mbox{CaH}_{2}(\mbox{CO}_{3})_{2} & + & 2\mbox{Na}_{3}\mbox{PO}_{4} & = & \mbox{Ca}_{3}\mbox{P}_{2}\mbox{O}_{8} & + \\ & & \mbox{sodium bicarbonate} \\ & & \mbox{}_{6}\mbox{Na}\mbox{HCO}_{3} \end{array}$

SOFTENING WITH SODIUM FLUORIDE

Calcium bicarbonate + sodium fluoride = calcium fluoride + $CaH_2(CO_3)_2$ + 2NaF = CaF_2 + sodium bicarbonate $2NaHCO_3$

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SOFTENING WITH SODIUM ALUMINATE

Calcium bicarbonate + sodium aluminate + water = $CaH_2(CO_3)_2$ + $Na_2Al_2O_4$ + $2H_2O$ = sodium carbonate + calcium carbonate + aluminum hydrate Na_2CO_3 + $CaCO_3$ + $2AlO_3H_3$ SOFTENING WITH SODIUM STEARATE (SOAP) Calcium bicarbonate + sodium stearate = calcium stearate + $CaH_2(CO_3)_2$ + 2NaSt = $Ca(St)_2$ +

sodium bicarbonate

2NaHCO3

The preceding experiments deal with hardness due to chalk or calcium carbonate, "limestone hardness," as distinguished from that due to calcium sulphate or "gypsum hardness." A hard water containing calcium sulphate can be made by gradually adding a halfteaspoonful of plaster of Paris to two tablespoonfuls of water contained in a mortar and grinding them together to form a thin paste. It is occasionally ground for an hour, put into a bottle with a pint of water, and allowed to stand for a day or two with occasional shaking. The same experiments may be tried with this solution as with the foregoing solution of bicarbonate of calcium.

Effect of boiling. Note that on boiling little or none of the calcium sulphate is precipitated. If it were possible for you to heat it up in a sealed glass tube to 280 degrees Fahrenheit it would be practically all precipitated.

Effect of lime-water. Note that lime-water produces no precipitate in the calcium-sulphate solution as it did with the bicarbonate-of-lime solution.

Effects of soda ash, sodium phosphate, fluoride, aluminate, and soap. Note that these are practically the same as with water containing calcium carbonate. If a solution of magnesium bicarbonate or sulphate were used the results would not be essentially different from the lime salts here used.

Experiments Illustrative of Corrosion and Pitting of Iron

1. Effect of pure water on iron out of access of air. Fill a 250-cc. flask, of the shape shown in Fig. 4, p. 19, two-thirds fulls of freshly distilled water, heat it to boiling and keep it gently boiling for thirty to forty-five minutes, tip it on its side without pouring out the water and *slide* into it two or three bright steel wire nails which have been carefully wiped free of any oil or dust; cork quickly with a soft, tight-fitting cork and allow to stand a few days. If the experiment has been properly performed the nails will remain bright.

2. Effect of pure water on iron with access of air. Repeat experiment No. 1 without corking the flask. Note the rapidity with which the iron is rusted.

3. Effect of various salts contained in natural waters on iron. Fill a number of 6-in. test-tubes two-thirds full of the following, one tube of each being sufficient: the "clear solution" of calcium bicarbonate, the solution of gypsum or plaster of Paris, these representing hard waters; ordinary well water, distilled water or rain water, or soft waters; a decoction of strong boiled tea or infusion of peat as representing peaty waters, distilled water with about one gram ¹ each of common salt, niter, and sal ammoniac, representing polluted waters; and of quicklime, soda ash, caustic soda or potash (Babbitt's lye) (Be careful), trisodium phosphate, sodium aluminate, fluoride, or any boiler compound as representing water softeners or boiler compounds. Incline the tubes as much as possible without spilling the water, and *slide* into them two bright clean steel wire nails as above. Observe and note the action on the nails, half an hour, one hour, three hours, and five hours after inserting the nails; let the tubes stand for a few days, and note the results, recording them morning and evening. The results of experiments made in the author's laboratory are shown in Table V.

Effect of metals, coke, scale, etc., on the corrosion of iron. Bind lightly together by means of a piece of florists' wire, two bright, clean, steel wire nails, and with one end of the wire still attached to them, wind the other end around a small piece of electric-light or dynamo-brush carbon, leaving perhaps four inches of wire between them. Put the nails and carbon into a 250-cc. beaker or half-pint wide-mouthed bottle or tumbler of clear glass, keeping them separate, and cover them about two inches deep with tap water, leaving the wire exposed.

Repeat this experiment, using instead of carbon a lump of soft or hard coal, some iron hammer or forge scale, a piece of copper, another of brass, a bit of zinc or aluminum, and two other nails.

¹ One gram represents a lump twice the size of a pea.

TABLE V

RESULTS OF EXPERIMENTS MADE TO SHOW THE RUSTING OF STEEL NAILS IN ARTIFICIAL HARD AND POLLUTED WATERS, AND IN BOILER COMPOUNDS

DESCRIPTION OF WATER	CONDITION AT TIMES SPECIFIED								
OF WALLA	$\frac{3}{4}$ hr.	$\frac{3}{4}$ hr. $1\frac{1}{2}$ hrs.		3 days	6 days				
Lime	Bright	Bright	Bright	Bright	Bright				
Gypsum	Slight rust	More rust	Very slight rust	Some rust	Considerable				
Bicarbonate of lime	Bright	Bright	Very slight rust	Slight rust	rust Some rust				
Tap (Boston)	Slight rust	More rust	More rust	Less than No. 2	About $\frac{1}{2}$ that				
Distilled	Slight rust	More rust	Rust spots	Less than	About ² / ₃ that				
Peaty	Bright	Bright	Bright	Veryslight	Very slight				
Salt	Bright	Very slight rust	Very slight rust	Rust	About 3 No. 2				
Niter	V slight rust	Slight rust	Bad spots	About twice No. 2	About $1\frac{1}{2}$ No. 2				
Sal ammoniac	Slight rust	More rust	Very slight	as No. 2	as No. 2				
Carb. soda	Bright	Bright	Bright	Bright	Bright				
Caustic soda Aluminate	Bright	Bright	Slight pits.	Bright	Bright				
soda	Bright	Bright	Slight pits.	Bright	Bright				
Phosphate									
soda (tri.)	Bright	Bright	Slight pits.	Bright	Bright				

As illustrating pitting, prepare a half-dozen pieces of bright iron or steel as large as a quarter, but square: in the center of each of these place a bit of hammer or forge scale, a piece each of coal, electric-light carbon, and copper, a bit of zinc and a small piece of the same iron. Put them all in an enameled iron hand-basin, into which a stream of tap water as large as a knitting needle is constantly flowing, and let them stand for two or three weeks.

The experiment with nails coupled with carbon, zinc, coal, etc., as carried on for six days in the writer's laboratory, showed:

With zinc very little action.

With nails some action.

With coal about twice the action with zinc.

With carbon about four times the action with zinc.

With copper about thrice the action with zinc.

This shows the protective effect of the zinc and the opposite action of the coal, copper, and arc-light carbon.

Practically the same results were obtained in two weeks with the iron squares: all were more or less rusted by the exposure; but the pitting was very marked with the arc-light carbon, the coal, the copper, and the hammer scale.

Tests to be Applied to Feed-Waters

Boiling Test. Boil a test-tube two-fifths full of the water: if a white powder or precipitate appears, it indicates bicarbonate of lime or magnesia.

Soda Ash Test. If, after the above boiling, the water remains clear, add a quantity of sodium carbonate (soda crystals or soda ash) as large as half a pea, and continue boiling: a white precipitate indicates the presence of gypsum or sulphate of lime, or possibly magnesium sulphate (Epsom salts).

Alcohol Test. Add to one-fifth of a test-tubeful of
water double its volume of the strongest alcohol obtainable, 90 per cent. or over: a white precipitate shows the presence of sulphate of lime; if slightly milky, about 250 parts per million are present; if a "good" test, about twice this amount.

Silver Nitrate Test. Add to one-half a test-tubeful a few drops of silver nitrate: a precipitate indicates chlorides and carbonates. Add a few drops of chemically pure nitric acid, when, if the cloudiness or precipitate be due to carbonates, it will clear, leaving that due to chlorides. Chlorides, as already explained, are corrosive agents, and come from rock-salt deposits and seawater.

With the exception of the boiling test, it may be necessary to boil down or evaporate the water in a porcelain dish to one-half or three-fourths of its original volume.

If the total amount of lime and magnesia compounds calculated as carbonate, sulphate, and chloride, as shown by a chemical anlysis of the water, be between 137 and 258 parts per million, the water may be classed as "good"; if from 258 to 344 parts, the water is only "fair."

The analysis of scale has already been given on p. 38.

VI

MINERAL OILS

THE mineral oils are, chemically speaking, hydrocarbons, *i.e.*, bodies composed of carbon and hydrogen, and as such are the least liable to change or "gum" of any of the oils. They are obtained by distilling crude petroleum or rock oil, usually a dark-colored strongsmelling liquid.

Several theories have been proposed as to the origin of petroleum: one is that it was formed from the flowerless plants and simple animals at about the same timeand in a similar manner as was coal; another that it was produced by the natural distillation of the fat of the fish that were so abundant just subsequent to the coal period. Professor Engler has substantiated this theory by distilling half a ton of menhaden oil at a pressure of 150 pounds and obtaining a product resembling crude petroleum, from which, by distillation, a good illuminating oil was prepared.

Petroleum is found in many localities, of which those in Pennsylvania, Ohio, Ontario, and Russia are the most important. It is obtained by drilling a well like an Artesian well, until the oil-sands are reached, usually at a depth of 1800 or 2000 feet, whence the oil gushes for a time and afterward requires to be pumped. Such a well costs about \$3500 and may yield a few or several hundred barrels per day.



FIG. 35. - Cheese-box Still. Cross Section

Lubricating oils are prepared by distilling off from the crude petroleum the lighter or more volatile portions, as the naphthas, kerosenes, etc., leaving the



FIG. 36. - Plan of Cheese-box Still

heavier portions. These latter in some cases require no further treatment, forming the "reduced oils"; or

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they are distilled, treated with sulphuric acid, and washed with soda and water, forming the "distilled oils."

The process of distillation ¹ is effected in huge upright or "cheese-box" stills (Figs. 35 and 36) 30 ft. in



FIG. 37. — Horizontal Still

diameter and 10 ft. in hight, of boiler iron, holding about a thousand barrels: horizontal stills (Figs. 37 and



38) 30 ft. in length and 10 ft. in diameter, containing 600 barrels, are often employed. These are heated by coal

¹ The process of distillation consists in changing the substance distilled to vapor, and chilling or condensing this vapor: an ordinary steam boiler is a still; "returns" serve as a condenser; and the "drip," or condensed water, as "distilled water." Distillation is a common method of separating, or purifying, liquids of different boiling-points, as alcohol and water, or the mixture contained in crude petroleum. fires and supplied with superheated steam to aid in carrying the heavy oil vapors rapidly out from the still. These vapors pass into iron coils or condensers (Fig. 39) where they are condensed to a liquid: according to the specific gravities of these liquids or distillates they are classed as gasolenes, naphthas, kerosenes, etc. The residue remaining in the large still is transferred



FIG. 39. - Condenser

to cylindrical cast-iron stills and distilled from soda solution, yielding finally kerosenes, "mineral sperm," and the various grades of engine oils, cylinder oils, vaseline, and heavy greases.

The refining process consists in removing the odor and the tarry matters formed in the process of distillation, and in improving the color: it is effected by agitating the oil in tall tanks with sulphuric acid, using compressed air, or in the case of the lighter distillates, mechanical stirrers. The oil is allowed to stand to separate the tar and sulphuric acid, the latter is drawn off, and the oil washed with soda solution and finally with water. The color of oils is removed by the acid treatment followed by sunning, and in the case of the lubricating oils by filtration through bone charcoal after the manner of sugar syrups.

Table VI shows some of the principal products derived from petroleum, together with their properties and uses.

Name	Gravity, Degrees B.	Boiling-point, Degrees F.	Use	
	N	APHTHAS		
Cymogene Rhigolene Petroleum ether Gasolene Naphtha Ligroine Benzine	110-100 100- 90 90- 80 80- 75 76- 70 67- 62 62- 57	32 65 100-150 150-190 160-210 160-225 225-300	Ice machines Anesthesia Gas machines Oil extraction Automobiles Stoves For turpentine	
	BURNING OILS Fire test			
Export oil Export oil Kerosene Mineral sperm	57- 53 53- 50 50- 47 39- 36	110 120 135–150 300	Burning (China) " (England) " (America) " (cars and boats, lanterns)	

TABLE VI

MINERAL OILS

LUBRICATING OILS

Name	Gravity	Flash	Cold Test	Viscosity
Spindle oils:	Deg. B.	Deg. F.	Deg. F.	Seconds
No. 4 Eagle	34.4	320	25	72 at 70°F.
No. 1 Eagle	30.3	_ 390	25	200
Engine oil	31.7	300	30	49
Engine oil	27.9	350	32	104
Engine oil	24.9	395	32	220
Bayonne engine oil	23.1	415	34	400
Cylinder oil	28.1	500	50-55	117 at 212°F.
Cylinder oil	27.5	550	50	150
Cylinder oil	26.1	600	35	200

Testing of Mineral Lubricating Oils. — The tests which it is feasible to perform outside a well-equipped laboratory are: viscosity, specific gravity, cold test, flash test, fire test, gumming test, acidity, for animal and vegetable oils, and for "oil-pulp."

Viscosity Test. By viscosity we understand the degree of fluidity of an oil or its internal friction; or its "body" or "greasiness" as it is sometimes expressed. Other things being equal, the least viscous oil should be chosen, or, otherwise expressed, the most fluid oil that will stay in place and do the work. A case is on record in which the changing of a spindle oil to one slightly more viscous caused the stopping of an engine and hence the whole mill, due to the increase in friction. Within certain limits, it may be taken as the measure of the value of an oil as a lubricant, particularly if the viscosity of the oil under examination

be compared with that of other oils which have been found to yield good results in practice.

The instruments employed for the determination of viscosity are constructed upon two different principles: one depending upon the time required for a certain quantity of the oil to flow through a standard orifice, as the Saybolt, Tagliabue, Redwood, and Engler; and the other, upon the degree to which a disk is hindered in rotating, by the viscosity of the oil, as the Doolittle.

The Saybolt apparatus, which may be taken as a type of the orifice instruments, will be described here. It is made in three forms, A, B, and C. Apparatus "A" is the standard for testing at 70 deg. F. Atlantic Red, Paraffin, and other distilled oils; "B" for testing at 70 deg. F. black oils of 0, 15, 25, and 30 degrees Cold Test, and other reduced oils up to, and not including, Summer Cold Test oil; and "C" is used for testing at 212 deg. F. Reduced, Summer, Cylinder, Filtered Cylinder, XXX Valve, 26.5 deg. B., and other heavy oils. The results are reported in seconds.

Apparatus "A," — Description. — The "A" apparatus (Fig. 40)¹ consists of a brass tube T, containing about 66 cubic centimeters, and about three centimeters in diameter and eight centimeters long, forming the body of the pipette. It is connected at the bottom with a smaller tube t, having a window w. This pipette is screwed into the piece p carrying the jet, 1.75 millimeters in diameter; the lower part of this piece is expanded at the bottom to admit of the insertion of a

¹ This, as well as some other tests, is taken from the writer's "Short Handbook of Oil Analysis."

cork. The upper part of the pipette is perforated with a number of small holes leading to a gallery G, 5 cm. in diameter and 1.3 cm. deep. This enables a workman to fill the apparatus to the same point every time. The pipette is held by p in a tank of water 18 cm. high and 20 cm. in diameter, also provided with windows to observe the efflux of the oil. A tin cup with spout,



FIG. 40. — Saybolt Viscosimeter

thermometer, pipette with rubber bulb, stop-watch, and beaker for waste oil, complete the outfit.

Having the bath of water prepared at 70 deg. and the oil in the tin cup about 69.5 deg., clean the tube out with some of the oil to be tested by using the plunger P sent with the instrument. Place the cork airtight in the lower outlet tube and pour the oil into the tube proper until it flows into the overflow cup.

By stirring with the thermometer, bring the oil to exactly 70 deg., remove the thermometer, and draw with a pipette the surplus oil in the overflow cup down below the overflow holes. The temperature still remaining constant, with the watch in the left hand, draw the cork with the right, and simultaneously start the watch. Toward the end of the run, watch the peep-hole closely through the window in the bath, and at the first appearance of space not filled with oil in the glass outlet, stop the watch. The number of seconds that have passed between the starting and stopping of the watch is the viscosity of the oil.

Specific Gravity. By specific gravity we understand the weight of a substance compared with the weight of an equal volume of water. The specific gravity of iron is 7.8: this means that a cubic inch of iron weighs 7.8 times as much as a cubic inch of water. In accurate work, attention has to be paid to the temperature. In the case of oils, the specific gravity is expressed in terms of the Baumé (pronounced "Bomay") scale for liquids lighter than water. This is an arbitrary scale in which water counts as 10 degrees. For example, a 76-deg. naphtha, a 25-deg. lubricating oil, means that the Baumé hydrometer would sink in the naphtha to the seventy-fifth degree and in the lubricating oil to the twenty-fifth degree, both these liquids being cooled to 60 deg. F. The mineral oils are usually designated by the Baumé scale, while the animal and vegetable oils are spoken of in terms of specific gravity:

cottonseed oil has a gravity of 0.922, meaning that a quart of cottonseed oil is nine hundred and twenty-two thousandths as heavy as a quart of water. The chief value of the test is to characterize the oil. This is usually effected by the hydrometer. A hydrometer jar



FIG. 41. — Baumé hydrometer

is four-fifths filled with the oil, a Baumé hydrometer (Fig. 41) introduced into it, and the depth to which the instrument sinks in the oil (Fig. 42) read off. This may be effected by placing a strip of white paper back of the jar and noting the point at which the lower

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meniscus or curve of the surface of the oil touches the scale, as at 20 deg. as shown in the figure. The temperature of the oil is taken at the same time, and in case it be not 60 deg. F. (15.5 deg. C.), for every increase of 10 deg. F. (5.5 deg. C.), subtract 1 deg. B. from the hydrometer reading. The specific gravity may be found by the formula $\frac{144.3}{134.3 + B^{\circ}}$, B° represent-



FIG. 42. — Stem of Baumé Hydrometer

ing the reading Baumé. In practice this reduction can be done by Tagliabue's "Manual for Inspectors of Coal Oil."

It is possible that the Saybolt viscosimeter cannot be obtained, in which case recourse must be had to Engler's or other viscosimeters. Instructions for using the apparatus accompany it.

Cold Test. This may be defined as the temperature

MINERAL OILS

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at which the oil will just flow. The importance of this test is seen wherever oils are exposed to freezing temperatures, as for example in railroad use on car axles: if the oil be chilled it ceases to flow and the bearing becomes hot; or, as has happened on the East Prussian railroad, the freezing of the oil in the axle-boxes stops the running of the trains.

The apparatus required comprises: a four-ounce vial; a thermometer; a quart can; and a freezing mixture.

The four-ounce vial is one-fourth filled with the oil to be examined, a short, rather heavy, thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the bottle to the other. The reading of the thermometer is now taken by withdrawing it and wiping off the oil with waste to render the mercury visible.

The chilling-point is the temperature at which flakes or scales begin to form in the liquid, and is determined similarly, by cooling the liquid five degrees at a time.

As freezing mixtures, for temperatures above 35 deg. F. use cracked ice and water; between 35 and 0 deg. F. use two parts of ice and one part of salt; and from 0 to 30 deg. F. use three parts of crystallized calcium chloride and two parts of fine ice or snow. A still more convenient means is by the use of solid carbonic acid, "carbonic acid snow," dissolved in ether or alcohol, giving -50 deg. F. readily.

Flash-Point. By flash-point is understood that temperature at which an oil gives off vapors in sufficient quantity to explode when mixed with air: this point is reached by burning oils in testing when a blue flame passes entirely over the surface of the oil; in



FIG. 43. — Flash-point apparatus for Lubricating Oils

lubricating oil, when a puff of flame comes out of the testing-hole in the cover. Like specific gravity, the chief use of the test with lubricating oils is to ascertain if any change has been made in the oil supplied. With burning oils it determines the safety of the oil. In considering the results of this test, differences of five to seven degrees F. may be disregarded, as duplicate tests upon the same sample may vary as widely as this.

Several forms of apparatus for testing the flash-point of lubricating oils have been devised: Pensky-Martens' closed tester employing a stirrer is used in Germany.' Martens states in a later article that stirring is unnecessary. Dudley and Pease use an open porcelain dish heated with a Bunsen burner. The apparatus in use in the author's laboratory is similar to the New York State tester, and consists of a covered copper cup shown at about one-tenth the size in Fig. 43 and drawn to scale in Fig. 47 (see Appendix, page 188), supported by gauze upon an iron stand and heated by a Tirrill burner.

The cup is filled with oil to within $\frac{3}{8}$ -inch of the flange (in case of cylinder or oils flashing above 500 degrees, $\frac{1}{2}$ -inch), all air-bubbles removed by pricking with a pointed stick, the flange and top of cup carefully wiped free of oil, the cover put on, and the thermometer inserted so that its bulb is half-way between the surface of the oil and the bottom of the cup. The lamp, carrying a flame about an inch in hight, is placed underneath, the bottom of the cup being two and one-half inches from the mouth of the burner, and the heating commenced. The rate of heating should be 15 deg. F. per minute, and may be easily regulated by the burner used. The testing flame should be first applied at 250 deg. F., and then every half-minute until the flashpoint is reached. This is indicated by a slight puff of flame out of the testing-hole. The results obtained with this apparatus agree better among themselves than those obtained with the open tester; they are usually 15 to 25 degrees lower.

Fire Test. The fire test is that temperature at which an oil gives off vapors in sufficient quantity to burn continuously when a flame is applied. The cover is supported above the cup, and the heating and application of the testing flame continued as in making the flash test.

The method of recording is the same as in the case of the illuminating oils, one column for times and another for temperatures. Holde finds that with oils flashing between 340 and 465 degrees F. the exact quantity of oil used is of little importance. In these particular cases a difference of filling of thirteen cubic centimeters altered the flash-point only two or three degrees F.

It is worthy of notice that the free acid (oleic acid) contained in an oil lowers its flash-point apparently in proportion to the quantity present.

Gumming Test. This is designed to give an idea of the amount of change that may be expected in a mineral oil when in use. These resinified products increase the friction of the revolving or rubbing surfaces. The test is applied by thoroughly mixing and beating together 5 grams of the oil in a cordial glass or small wide-mouthed bottle with 11 grams of nitrosulphuric acid, and cooling by setting the glass in a basin of water at 50 to 60 degrees F. Brownish spots or, in case of a bad oil, masses form around the edges and gradually cover the whole surface in the course of two hours. As

shown by long practical experience, the oil showing the least tar is the best oil and also absorbs the least oxygen.

Nitrosulphuric acid is troublesome to prepare; but directions therefor will be found in the writer's "Handbook of Oil Analysis," and it may be replaced by nitric acid and copper. Use ordinary nitric acid, 1.34 sp. gr., drop into this two pieces of No. 15 B. & S. gage copper wire ³/₄-inch long, and in an hour two more pieces.

Test for Acidity. In a petroleum oil the acid present is usually sulphuric, owing to the acid used in refining being incompletely washed out of the oil. Its presence can be detected by shaking about one-fourth of a test-tubeful of oil with an equal quantity of warm distilled water in a test-tube. The oil is poured off carefully, and the water tested with neutral litmus paper, which in presence of acid is changed to red. If the litmus paper used were too blue, the acid might be all used up before the color changed; hence in this case it should be exposed to the fumes of hydrochloric acid until nearly neutral. A test should be made to be sure that the water is not acid. Not more than a faint reddening is allowable: the acid content should not exceed 0.3 per cent., calculated as sulphuric anhydride (SO₂).

Test for animal and vegetable oils in mineral oils. Put about an inch of the oil into each of two test-tubes; add to one of these, two pieces of metallic sodium as large as half a pea and to the other a similar quantity of sodium hydrate (caustic soda). Extreme care should be taken in handling these substances as the metallic sodium takes fire if wet, forming caustic soda which attacks the skin and clothing vigorously: if any gets upon either, wash it off with water and dilute muriatic acid, and the acid with water. Heat the test-tubes in an oil bath, that is, an iron pot containing heavy cylinder oil, lard, or cottonseed oil, deep enough to cover the oil surface in the tube to a temperature of about 445 deg. F., in case the oil be a light-colored one, and to 480 deg. F. if it be dark-colored. In case fatty oil be present, the contents of one or both of the tubes show a foam as of soap bubbles on the surface, and solidify to a jelly of greater or less consistency according to the amount of fatty oil present.

Detection of "oil-thickener" or "oil-pulp." This is usually an oleate of aluminum, a soap, which is dissolved in the oil to increase its viscosity at ordinary temperatures, but has little effect on the oil at the temperature at which it is used. It may be detected by diluting the oil with an equal quantity of naphtha and adding about 15 drops of a saturated solution of stick phosphoric acid in absolute (100 per cent.) alcohol. The mixture is allowed to stand, when the formation of a flocculent precipitate indicates the presence of soap.

As showing the extent to which it affects the viscosity, a sample of oil containing it would not flow from the viscosimeter at 70 deg. F., required 1167 seconds at 85 degrees and 181 seconds at 110 degrees.

A test which is often applied to light oils, like spindle and loom oils, is the evaporation test: this measures

the loss sustained by an oil when exposed on a bearing. It requires a delicate analytical balance, sensitive to $\frac{1}{10}$ milligram (0.0015 grain), to detect the loss, as the amount of oil used is small (200 milligrams). The amount of loss should not exceed 4 per cent. The test is important to the mill-owner as it represents the amount of oil that stays on the bearing and serves its purpose. It is of even greater importance to the insurance underwriter, as it measures the amount of volatile inflammable matter passing into the atmosphere and liable to cause a fire. This actually happened in a spinning-mill in Maine: the oil contained, however, 25 per cent. of volatile matter; that is, the evaporation test was 25 per cent. As a result of an investigation undertaken by the Boston Manufacturers' Mutual Fire Insurance Company, all oils of this type were driven out of use within a year.

Specifications for Lubricants. There seems to be a tendency, more particularly in England, not to use specifications in purchasing oils. Taggart ¹ makes the following rather remarkable statement: "At present one seldom meets with such a specification and it is certainly of little credit to the engineer who issues one. To the manufacturer of the oil it may be important, but to the engineer it is useless and the wise ones are beginning to realize the fact." The fact is that the manufacturers control their product by these very chemical and physical tests; if they are "important" to the manufacturer, they certainly are of equal importance to an engineer, who should be "wise" enough

¹ Power, July, 1906, page 434.

to know what they mean and how they are applied. This is in line with the remark of an oil dealer to the author that a course of instruction in oil testing was going to make his work more difficult.

The writer is inclined to believe that the objection to specifications for oils is fostered by certain oil com-



FIG. 44. — New York State Tester

panies, and he finds it difficult to believe that it is not for ulterior purposes.

Specifications for lubricants are issued by many railroads, both in America and in Germany, and by textile, paper, brass, iron, steel and other manufacturers, also by municipalities for their water works and elec-

tric light plants; in fact, they are employed by nearly all large users of oil. The introduction of specifications is usually followed by a decided drop in the expense for oil. Specifications, particularly for oils for railroad work, will be found in the author's "Handbook of Oil Analysis," and pp. 180 to 182 of this book.

Testing of Burning Oils. The chief tests to be applied to this class of oils are the flash and fire tests, specific gravity and sulphuric acid test.

In making the *Flash Test*, three different types of testers are used: (1) the open or Tagliabue tester, in which the cup containing the oil is not covered or closed, but is freely open to the air; (2) the covered or New York State tester, in which the cup is covered with a glass cover containing two holes; and (3) the closed or Abel tester in which the oil is heated in a tightly closed cup which is opened momentarily for the introduction of the testing flame.

The New York State tester consists of a copper oil cup D (Fig. 44), holding about 10 ounces (the quantity usually contained in a lamp) and heated in a waterbath by a small Bunsen flame. The cup is provided with a glass cover C, carrying a thermometer B and a hole for the insertion of the testing flame — a small gas flame $\frac{1}{4}$ -inch in length.

The regulations of the New York State Board of Health ¹ stipulate that the test shall be applied according to the following directions:

"Remove the oil-cup and fill the water-bath with cold water up to the mark inside. Replace the oil-cup and pour in enough oil to

¹ Report of the New York State Board of Health, 1882, page 495.

fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air-bubbles with a piece of dry paper. Place the glass cover on the oil-cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

"If an alcohol lamp be employed for heating the water-bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

"As a flash-torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed linen twine. The flame in this case, however, should be small.

"When the temperature of the oil has reached 85 degrees Fahr., the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to clear well the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every two degrees' rise of the thermometer until the thermometer has reached 95 degrees, when the lamp should be removed and the testings should be made for each degree of temperature until 100 degrees is reached. After this the lamp may be replaced if necessary and the testings continued for each two degrees.

"The appearance of a slight bluish flame passing entirely over the surface of the oil shows that the flashing-point has been reached.

"In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

"The water-bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil-cup."

In making the flash test it should be borne in mind that any cause liberating the vapor quickly from the oil lowers the flash-point: such causes are: (1) rapid heating; (2) a large and shallow cup from which the

evaporation takes place quickly; (3) a large quantity of oil used for the test; and (4) a large testing flame or one too frequently or closely applied.

The results obtained with this apparatus are about five to eight degrees lower than those obtained with open cups. This cup reproduces more closely than any other the conditions prevailing when burning the oil in lamps. The amount of oil used is about 10 ounces, the capacity of an ordinary lamp: the tester, like a lamp, is not freely open to the air, preventing the escape of volatile vapors. This escape takes place with open cups and consequently the results obtained with them are higher.

The *Fire Test* is made by raising the cover above the cup and continuing to heat the oil until it gives off vapors which burn continuously when ignited. It is usually 15 to 25 degrees higher than the flashpoint.

In choosing a burning oil, one of a high flash-point rather than one of a high fire-point should be selected, as the flash- not the fire-point determines the safety of the oil. Oils having a high flash test are sure to have a high fire test; but those of a high fire test may or may not have a high flash test. That is, in only making the fire test, no attention is paid to the flash test, and the dangerous volatile constituents of the oil (naphtha) escape detection, being driven off. This was well illustrated in a sample of fuel oil sent to the writer for test. The flash-point was 60 deg. F. and the fire-point 143 deg.: had the fire-point alone been considered it would have been regarded as a safe oil, whereas the flash-point (60 deg. F.) showed it to be dangerous. Too much stress, therefore, cannot be laid on the flash test, which should be at least 110 deg. F. (or better, 120 deg. F.), remembering that a safe oil makes safe lamps. Professor Engler states that no lamp should be used which heats the oil more than 10 deg. F. above the surrounding atmosphere.



FIG. 45. — Thurston's Oil Friction Testing Machine

The *Specific Gravity* of burning oils is determined exactly as in the case of lubricating oils.

The Sulphuric Acid Test shows the degree to which an oil is refined, that is, the extent to which the tarry and ill-smelling products in the oil, or formed during the process of distillation, have been removed from the oil. It is made by shaking 100 grams of the oil with 40 grams of sulphuric acid of 1.73 sp. gr. for two minutes and noting the color of the acid layers: a suitably refined oil should give little or no color.

Friction Test. By this is meant the determination of the amount of power required to overcome the resistance of an oil when applied to a bearing. The oil



FIG. 46.— Thurston's Friction Testing Machine

is tested under ideal conditions, with a shaft and boxes as nearly perfect as mechanical skill can make them, with the feed of oil, the temperature of and pressure on the bearing even, regular, and under complete control.

The small Thurston machine shown in Figs. 45 and 46 will give an idea of the principle and construction

of these machines. It consists of the testing-shaft or journal F, $1\frac{1}{2}$ in. long by $1\frac{1}{4}$ in. in diameter, and the bronze bearings G G', the pressure of which on the shaft can be regulated by the coiled spring. The amount of pressure is shown by the index M: a thermometer in Q indicates the temperature of the bearing. The journal is rotated, by means of the step-pulley C, in the direction of the arrow; this causes a displacement of the pendulum G K, containing the spring J along the arc P P'.

The amount of displacement along this arc measures the friction of the oil, being large with great friction and small with good lubricants. The arc is so graduated that, dividing the reading by the pressure shown by the index M, the coefficient of friction is given. This machine is designed for testing the lighter oils: a larger size of this machine is made with journal $3\frac{1}{4}$ in. in diameter and 7 in. long for heavy lubricants and railroad work.

The writer is inclined to question the value of the friction test for practical purposes: he believes that equally good or better results can be obtained by comparing the flash, fire, gravity, and viscosity tests of the oil in question with those of one that has given satisfactory results in practice.

This holds strictly true only of oils coming from the same field or part of the country; Texas, Ohio and Pennsylvania oils, or oils having an asphaltic base, cannot be compared with those having a paraffin base, nor those carrying sulphur with those not carrying sulphur.

VII

ANIMAL AND VEGETABLE OILS — GENERAL CONSIDERATIONS REGARDING LUBRICANTS

The petroleum oils considered in the preceding chapter are, chemically speaking, hydrocarbons — composed solely of carbon and hydrogen — and as such, very stable bodies. Their formulas are very simple, represented by the general expression C_nH_{2n+2} . Yet a given oil, as for example 25-degree paraffin, cannot be represented by figures, as $C_{15}H_{32}$ in place of the *n* and n + 2 in the formula just given, the reason being that the petroleum products are mixtures of bodies having for the most part the formula given.

Besides containing $C_{15}H_{32}$ it most likely contains $C_{12}H_{26}$, $C_{13}H_{28}$, $C_{16}H_{34}$ and others up to $C_{20}H_{42}$, or even higher. The reason for this is, that the hydrocarbons given boil within a few degrees (27–36) of each other and cannot be separated in the ordinary process of distillation, very careful and numerous redistillations being required.

Animal and vegetable oils, besides being made up of carbon and hydrogen like the preceding, contain oxygen, and their formulas are by no means so simple as the petroleum oils; they are salts, organic salts of organic acids, resembling the inorganic salts we had in some of the early chapters. The base is usually CH_2OH

glycerin CHOH or C₃H₅(OH)₃, C₃H₅ being trivalent CH₂OH

like aluminum (Al), in Al(OH)₃, and the acid may be stearic ($C_{17}H_{35}COOH$), palmitic ($C_{15}H_{31}$ COOH), or oleic ($C_{17}H_{33}COOH$), and their union produces ($C_{17}H_{35}-$ COO)₃ C_3H_5 , stearine, ($C_{15}H_{31}COO$)₃ C_3H_5 , palmitine, forming the solid portions of fats, and ($C_{17}H_{33}COO$)₃ C_3H_5 , oleine, the liquid portion. These glycerides, as these compounds are also called, form the basis of most of the animal fats and oils, in which they are mixed in varying proportions. The differences in the fats or oils are produced partly by the different quantities of the glycerides named, but mainly by the admixture of small quantities of the glycerides of other acids, as butyric in the case of butter, linoleic and linolenic in the case of linseed, and other drying oils, etc.

That the fats and oils are really salts, as has been stated, can be seen from their behavior with caustic soda or potash, which converts them into soap, setting free glycerin at the same time:

 $\begin{array}{rl} (C_{17}H_{35}COO)_3C_3H_5 + \ _3NaOH &= C_3H_5(OH)_3 + \ _3C_{17}H_{35}COONa \\ & & (\text{sodium stearate}) \\ & & & \\ & &$

This class of oils is distinguished from the hydrocarbon or petroleum oils in being saponifiable (there is no known way of saponifying the petroleum products), and, when heated, in breaking up or "cracking" into

acid products, instead of distilling over as do the petroleums.

Vegetable oils are divided into two classes: the fatty or fixed oils and the volatile oils. The former cannot be distilled without decomposition, are not volatile with steam, and leave a fixed stain on paper or cloth. The volatile or essential oils distil readily, pass over with steam, and evaporate completely from paper: these are the bodies which give the characteristic odor or perfume to plants and flowers, as peppermint, rose, lemon, etc. Their composition is very complex, being mixtures of organic salts of organic acids similar to the fatty oils, as well as acids, alcohols, ketones, hydrocarbons, etc.; oil of peppermint contains no less than fifteen different compounds.

Oil is found in all parts of animals and vegetables, although more is contained in certain parts than in others. In land animals the fat occurs on the back, abdomen, and upper parts of the legs; in fish, around the body, as the blubber of the whale, in the head with the blackfish and sperm whale, throughout the whole body, as in the menhaden, and in the liver as with the codfish and shark.

With vegetables, oil is mostly found in the seed, although with the essential or volatile oils they occur in the flower as with the rose, in the bark as with cinnamon, and in the root as with sassafras.

These oils are contained in cells composed of animal membranes or cellulose, and to obtain the oil the cells must be ruptured; this is usually done by heat in the case of animal, and with vegetable oils by grinding and pressure. The membranes containing oil soon putrefy on standing, causing the oil to turn rancid and have a bad odor; consequently, animal oils should be rendered as soon as possible.

The animal fat is cut up into small fragments and filled into large digestors or autoclaves, heated with direct steam. The apparatus is filled and discharged by manholes at the top and bottom. On steam, at 50 pounds pressure, being admitted, the cell walls are broken down and the fat melted which flows, together with the water, to the bottom of the apparatus. The gases evolved, together with some steam which is condensed, pass to a chimney or sewer: after a few hours' heating the steam is shut off, the pressure removed, and the autoclave allowed to stand to separate the oil from the water: the separation can be determined by means of cocks at various heights upon the autoclave. When this has taken place, the water is drawn off as completely as possible through these cocks, and the oil through another. The animal tissue (cell walls or membranes), "scraps" or "cracklings" are discharged through the bottom manhole. These cocks serve also as exits for the water used in washing the fat after it is packed in the autoclave.

With the vegetable oils the seeds, hulled in some cases, are crushed by rollers or edge-runners, rupturing the oil-cells, the resulting mass being steamed or "cooked," to complete the rupture and render the oil more fluid, and then pressed in duck or horsehair bags, in a hydraulic press. This consists of a framework supporting the top against which the bags

are pressed by the ram, forced out of its cylinder by the pressure of water or oil which is pumped into it. Oil obtained by cold and moderate pressing is the best. The yield is small, and after pressing in this manner the press is inclosed and heated by steam, and the pressure increased with a corresponding increase in yield.

Besides these presses, wedge, screw, knuckle-joint, lever and eccentric presses are used.

As was noted in a preceding paragraph, vegetable oils can be prepared by dissolving them out from the crushed mass with naphtha, carbon bisulphide or tetrachloride. To this end the crushed seeds are filled into boiler-iron extractors like the autoclave, provided with false bottoms, and the solvent, as naphtha, caused to circulate through the mass, dissolving out the oil. The solution is then heated, the solvent distilled off, leaving the oil, and the condensed solvent can be used again. A larger yield of oil is obtained by this method, but it contains more impurities as gums, gelatinous matters, etc., for the naphtha dissolves these as well as the oil. Furthermore, the odor of the solvent is difficult to remove from the oil completely. The residue left in the extractors, containing less oil, is not as valuable for cattle feed as the press cake, and can only be used as a fertilizer or fuel. The plant for this process is more complicated and expensive, and more dangerous as a fire risk.

The oils as freshly expressed or rendered, are often dark in color or contain resinous, gummy, or gelatinous matter, fatty acids and water, and require to be refined or clarified. The treatment varies with the oil: with cottonseed, whale, and sperm oils they are treated with caustic soda lye which combines with the color and saponifies the fatty acids, the soap thus formed carrying down the gummy matters as "foots." Some of the animal oils, as lard, are in addition treated with compressed air and fuller's earth to improve the color. Certain other oils are bleached with acids and bichromate of potassium or sodium peroxide; oftentimes, as with linseed oil, water and mucilage are removed by allowing the oil to settle for twelve to eighteen months, becoming an "aged" or "varnish oil." Besides this artificial means, oils are bleached by exposure to sunlight in shallow tanks.

Examination of an Animal or Vegetable Oil. — In examining an unknown oil the analyst should ascertain all possible facts about it, its cost, its source, and the use for which it is intended. There is unfortunately no such number of specific tests for the various oils as there are for the various metals: while it is easy to say positively that a certain metal is present or absent, the same cannot be said of many of the oils. We can be absolutely sure of the presence of cotton-seed, sesame, palm, rosin and mineral oils, and reasonably certain of peanut, rape, castor, and sperm, but can only have more or less strong suspicions as to the presence or absence of most of the others.

The fact, too, that crops vary in quality from year to year, cannot but have its influence upon the quality of vegetable oils produced. Whereas in the case of an inorganic compound, like soda ash, we can require that

it must contain 58 per cent. of oxide of sodium, with less than 1 per cent. variation either way, we cannot prescribe such definite specifications for oils, for the reason just stated, *i.e.*, the variation in genuine oils, on account of the change due to the season, wet or dry, cold or hot, or the variety of the plant or tree - there are 300 varieties of olive-trees in Italy alone. These influences change the "constants," like the specific gravity, Maumené figure, etc., which are our guides for the determination of the amount of adulteration of an oil. For example, the Maumené figure for olive-oil varies from 35 to 47 degrees C.; consequently, if we find a figure of 44 degrees, there are three possibilities: first, that the oil is genuine; second, that it is an oil originally of a figure of 47 degrees which has been adulterated with an oil of lower Maumené figure; or, third, that the original figure was 41 degrees and it has been adulterated with an oil of higher Maumené figure. As to which of these is correct, we must be guided by other "constants" and special tests. There is a variation of $\frac{12}{44}$ or 27 per cent. in these "constants"; consequently, the determination of the percentage of one oil in another may not be accurate within about 14 per cent. On the other hand, it should be noted that the sensitiveness of chemical methods permits the carrying out of the processes for the determination of these "constants" within at least 1 per cent. or even less.

Considering the items of cost, source and use, the cost, compared with current prices, will give an idea of the kind of oil if it be uncompounded: it is not usual to find an expensive oil mixed with one of lower price, unless in certain lubricants. The source or kind of an oil will give an idea of the possible adulterants, and also of the tests and constants to which it should respond. If the source or kind of oil be not known, the use to which the oil is to be put is of material help in determining its composition: for example, the paint oils are linseed, menhaden ("pogy"), and, in some cases, corn; the currying oils are neatsfoot and "cod"; the burning oils, lard, sperm, and rape.

Tests for Animal and Vegetable Oils. — *Physical tests.* The smell of an oil reveals much to the expert regarding its composition; and if the amateur will take the trouble to make a collection of samples of genuine oils for comparison he will find them very valuable in this connection. The odor is best taken by warming the oil in a small beaker, or by rubbing a small quantity of the oil between the thumb and finger and smelling them. Marine animal oils are readily detected by their strong "fishy" odor, while neatsfoot, tallow, lard, olive, rosin, and linseed oils have each a well-marked and easily distinguishable odor. Many of the statements just made, apply with equal force to the taste of oils, rape oil having a harsh, unpleasant taste, and whale oil a nutty flavor.

The color of an oil is not to be relied upon for identification, as oils may be colored reddish or greenish by the oleates of iron or copper: the "bloom," fluorescence or peculiar bluish or greenish streak seen on the sides of a vial containing mineral oil, is proof positive of the presence of a hydrocarbon or petroleum oil; this can be further shown by putting a few drops of the oil on a piece of hard rubber or other black surface and observing the bluish color.

Specific Gravity. This is determined in the same way, with a hydrometer, as with mineral oils: if the instrument be graduated in Baumé degrees only, the reading should be converted into specific gravity referred to water, as that is the way in which the animal and vegetable oils are designated. Care should be taken to note the temperature of the oil, which should be 60 deg. F., as in the case of petroleum, and for every degree Fahrenheit above 60 add 0.00035 to the observed specific gravity. Suppose, for example, the hydrometer shows a reading of 23.75 deg. B. at 70 deg. F.: required the specific gravity of the oil in question at 60 deg. F.? According to Table X in the Appendix 23 deg. B. = 0.9150 and 24 deg. = 0.9090, a difference of 0.0060 for 1 degree Beaumé: 0.75 deg. B. the excess above 23 deg \times 0.006 = 0.0045. 0.9150 -0.0045 = 0.9105 deg. That is, 23.75 deg. B. = 0.9105 sp. gr. At 70 deg. F. for every degree Fahrenheit above 60, 0.00035 is to be added, or 0.0035 for 70 - 60= 10 degrees. 0.9105 + 0.0035 = 0.9140, the specific gravity of the oil at 60 deg. F. The fact that the hotter an oil is the lighter it is, should not be forgotten, and also the reverse of this statement. Table XI, Appendix, shows the specific gravity of certain oils also expressed in degrees Baumé, and their weights per gallon and per cubic foot.

Valenta Test. This depends upon the solubility of

the various oils in glacial acetic acid.1 Instead of determining how much acid is necessary to dissolve a certain quantity of oil, equal quantities of oil and acid are mixed, warmed, then cooled and the temperature at which the oils become turbid is noted. The test bears the name of the discoverer. To perform it, sufficient oil is poured into a test-tube to fill it about an inch in depth, the hight to which it rises being indicated by the thumb-nail, and a quantity of glacial acetic acid equal to the oil poured in upon it, until it reaches the hight shown by the thumb-nail. A rather light chemical thermometer - usually graduated in Centigrade degrees - serves to mix the oil and acid, and the mixture is heated over an alcohol or gas lamp until it becomes clear; it is allowed to cool and the temperature at which it becomes cloudy is noted; it is slightly warmed again until clear and the cooling is repeated. The readings should coincide within half a degree. Castor oil is soluble at the ordinary temperature, while rape seed is usually insoluble at the boilingpoint of the acid; the temperatures at which some oils become turbid are shown in Table XII, Appendix.

Elaidin Test. This test depends on the fact that certain oils, rich in olein, like lard and neatsfoot, are changed by nitrous acid into a solid body having the same composition — elaidin. It serves to distinguish between the non-drying, semi-drying, and drying oils: when submitted to this test, the non-drying oils usu-

¹ Glacial acetic acid is so strong that it freezes at 17 deg. C. and boils at 118 degrees Centigrade. Care should be used not to get it upon the person, as it blisters severely.
ally form a solid cake, so solid in fact that the vessel and contents can be lifted by the rod congealed in the cake of elaidin; the semi-drying oils form a more or less pasty mass, while the drying oils form a liquid mass with clots floating about in it. The test is performed as follows: five grams of the oil are weighed out into a cordial glass (a small goblet about three inches high) on the horn pan scales and seven grams (about 5 cc.) nitric acid of 1.34 sp. gr. weighed into it, and the glass immersed in a pan of iced water, at 50 to 60 degrees Fahrenheit, to within half an inch of the top. After about ten minutes two pieces of copper wire, No. 15, B. & S. gage, $\frac{3}{4}$ inch long are dropped in, and the oil and acid stirred together with a short glass rod, with an up-and-down as well as a rotary movement, so as to mix the oil, acid, and evolved gas thoroughly. When the wire has dissolved, add two more pieces and stir as before: this should furnish gas enough, if the liquid has been kept cool and the stirring has been thorough. At the end of the first hour pure lard will usually show flakes of a wax-like appearance, and upon standing without disturbance for another hour at the same temperature, the oil will have changed to a hard, solid, white cake. Most of the fish and seed oils yield a pasty or buttery mass separating from a fluid portion, whereas olive, lard, sperm, and sometimes neatsfoot oil, yield a solid cake. To make sure of the manipulation, a test should be made at the same time and in the same way with an oil of undoubted purity - lard oil for example: if a hard cake be obtained in the latter case, and a buttery mass with the oil under

examination, it is very good evidence that the latter is either a seed oil or an olive, lard, or sperm oil, adulterated with a seed or mineral oil.

The Maumené Test (pronounced Mómenay), or heating test with sulphuric acid, is one of the most important tests to determine the variety or kind of an oil: it possesses the advantage that it requires no complicated apparatus and is simple in execution. The underlying principle is, that when oils are mixed with strong sulphuric acid, heat is produced and the quantity of heat so produced is characteristic of the various oils.

The apparatus required consists of a rather tall and narrow beaker holding about five ounces (150 cc.) which is packed in a tin can, agate-ware cup or larger beaker, with dry cotton waste or hair felt, the packing being perhaps an inch thick; a light thermometer graduated from 0 to 150 or 200 deg. C., a 10-cc. graduate and pair of horn pan scales complete the outfit.

The test is conducted as follows: The beaker is taken out from its packing — disturbing it as little as possible — weighed on the scales, and fifty grams of oil weighed into it, to within two drops, the beaker replaced in its jacket, the thermometer inserted in the oil, and its temperature noted down. Ten cubic centimeters of strong sulphuric acid are measured out in the graduate and gradually run into the oil, it being stirred at the same time with the thermometer, and the graduate allowed to drain about five seconds—that is, while one counts ten. The stirring is continued until no further increase in temperature is noted. The highest point at which the thermometer remains constant for any appreciable time is observed, and the difference between this and the original temperature of the oil is the "rise of temperature."

The mixture of oil and acid is thrown on the ash-heap, the thermometer and beaker are carefully wiped free of oil with cotton waste; and the jacket is allowed to cool down to the original temperature, when the apparatus is again ready for use. A duplicate test should always be made and the results should agree within 2 or 3 per cent.: that is, with a rise of 40 deg. C. the results of the two experiments should differ only by one degree. Since the rise of temperature varies with the strength of the acid, to secure uniformity, the experiment should be repeated, using water instead of oil, and the rise of temperature here obtained, used to divide the rise of temperature with the oil, and the result multiplied by one hundred. This is called the "specific temperature reaction." The acid used should be the strongest obtainable and should show a specific gravity of 1.84. Fuming sulphuric acid should not be used.

In case the test is to be applied to a drying or semidrying oil, it should be diluted with an equal weight of petroleum oil and then thoroughly mixed: the "rise of temperature" is in this case the rise of temperature of the mixture, minus half the rise of temperature of fifty grams of mineral oil, multiplied by two.

For concordant results, the conditions should be the same, and the same apparatus should be used. The percentage of one oil in a mixture of two oils can be found by the following formula: Let x = percentage of the one oil and y of the other; further, m =Maumené value of pure oil x, and n of pure oil y, and I of oil under examination, then $x = \frac{100(I - n)}{m - n}$

To illustrate the application of this formula, suppose we have an olive-oil adulterated with cottonseed: the sample in question has a Maumené figure of 60. We see from Table XII, Appendix, that cottonseed oil has a Maumené figure of 76 and olive-oil one of 35. Then, substituting in the formula, $x = 100 \left(\frac{60 - 35}{76 - 35}\right) = 61$ per cent. That is, there is about 60 per cent. of cottonseed oil in the olive-oil. As with other oils, it is advisable to make a test with an oil of known purity.

Halphen's test for Cottonseed Oil. This depends upon the fact that this oil contains a fatty acid, which combines with sulphur giving a colored compound. The apparatus needed is a large test-tube seven or eight inches long by one inch in diameter, fitted with a tube $\frac{3}{8}$ inch in diameter and about five or six feet long, to serve as a condenser for the alcohol which is used in the test. To join or fit the long tube to the test-tube, soften a good cork that fits the testtube, by rolling it under a board on the bench: with a 6-inch or 7-inch round file, bore a hole through the cork from the small end, file this out using larger round files until the long tube fits snugly-into the cork. Before trying the tube in the cork, round the sharp edges with a file, otherwise they will cut the cork and make a poor fit; if the tube be wet, it will slip or twist into the cork much better. Besides this, an agate-ware

cup holding brine, and means of heating it, and a waterbath are required. The chemicals or reagents needed are amyl alcohol (fusel oil) and a $1\frac{1}{2}$ -per-cent. solution of sulphur in carbon bisulphide. This should not be opened near a fire or flame, as it is very inflammable.

To make the test about two or three teaspoonfuls (10–15 cc.) of the melted fat or oil (the exact quantity makes no difference) are heated with an equal volume of the amyl alcohol and of the carbon bisulphide solution of sulphur, with occasional shaking, in the water-bath, and after the violent boiling has ceased, in the brine bath at about 220–230 deg. F. for forty-five minutes to three hours, according to the quantity of cottonseed oil present, the tube being occasionally removed and shaken. As little as I per cent. will give a crimson-wine coloration in twenty minutes. If the mixture be heated too long, a misleading brownish red color due to burning is produced.

Test for Unsaponifiable Oils in Animal or Vegetable Fats and Oils. This depends upon the fact that when a soap solution containing unsaponified oil is diluted with water, it is precipitated, causing an opalescence or turbidity. Six or eight drops of oil are boiled two minutes in a test-tube with a teaspoonful of 3-per-cent. alcoholic-potash solution: this is made by dissolving caustic potash in ordinary alcohol or wood spirits. The potash makes soap of the oil, and to this soap solution distilled water is gradually added ($\frac{1}{2}$ to 15 cc.), and one notices whether the solution remains clear or whether a turbidity appears which clears on the addition of more water: even 1 per cent. of mineral oil may be detected in this way.

There are two other tests which are applied to these oils which require considerable experience and a number of reagents that can be prepared only by a skilled chemist: as these are sometimes referred to in oil analysis they will be defined here. These tests are the *Saponification Number* and *Iodine Value*. By the saponification number or value is meant the number of milligrams of potassium hydrate (KOH) necessary to saponify one gram of the oil: this is nearly the same for many oils, averaging 193; rape has a number of 178, and sperm 124–145. The number is mainly of value in detecting adulteration of animal or vegetable oils with petroleum or rosin oils which are not saponifiable.

By the iodine number or value is understood the number of milligrams of iodine absorbed by one gram of oil; this varies from 176 with linseed to 8 with cocoanut oil. This can be used the same as the Maumené figure for calculating the adulteration in an oil.

The tests to be applied to animal or vegetable oils may be summarized as follows:

Ascertain, if possible, source, intended use, and cost. Note color, sediment, and bloom.

Compare odor and taste with genuine samples.

Determine specific gravity with hydrometer (be careful about temperature).

Make the Elaidin and Maumené tests, and calculate from the latter the percentage of each oil present.

If cottonseed be suspected, apply the Halphen test.

Source, Properties and Uses of Some of the more Important Animal and Vegetable Oils.

Castor oil is obtained by pressing castor beans which contain about 50 per cent. of oil. It is a colorless or pale-greenish, heavy, thick, and viscous oil. It is adulterated with blown oils (for few others are heavy enough to serve as adulterants), such as linseed, rape, or cottonseed and rosin oils. These, though 10 per cent. be present, cause a turbidity with alcohol with which castor oil is miscible in every proportion. Castor oil is employed in medicine, in the manufacture of Turkey-red oil ("sulphonated oil"), for soap-making, illumination, as a belt dressing and on steamships as a lubricant.

Corn or maize oil is obtained by pressing the germ of the corn separated in the manufacture of starch or alcohol: it is a pale to golden-yellow oil, excelling cottonseed oil in absorbing oxygen from the air. It is adulterated with mineral and rosin oils which would be shown by lowering the Maumené value and in the case of mineral oil by the lower specific gravity. It is used as an adulterant for linseed and lard oils, for painting, burning, lubricating and soap-making, and, after treatment with sulphur chloride, as a waterproof and belt dressing, and a substitute for rubber.

Cottonseed oil is prepared by pressing the seeds of the cotton plant, which contain about 25 per cent. of oil. When first pressed, it is ruby red or black, and is purified by treatment with caustic soda, carrying down the color and gelatinous substances as "cottonseed foots." The oil thus obtained varies in color from white to deep yellow. It belongs to the class of the semi-drying oils, slowly absorbing oxygen from the air and "gumming," which renders it less valuable as a lubricant. Cottonseed oil is rarely adulterated: it however serves to adulterate other oils, where its presence can be shown by the Halphen test, already described. Other uses are as a screw-cutting oil, for soap-making, and as a salad and cooking oil in "Cottolene," "Cotosuet," etc.

Horse oil is prepared by rendering dead horses. It varies in consistency from an oil to a grease, and in color from light to deep yellow. It is used for mixing with and adulterating other oils.

Lard oil is obtained by pressing lard. The lard is chilled, brought into press-cloths and pressed in screw or chain presses at a pressure of about four tons to the square inch, yielding from 40 to 60 per cent. of oil. The oil is valued according to color, which varies from reddish brown to very light straw yellow, according to the lard from which it is pressed: oftentimes the color is improved by refining with fuller's earth. The grades in the market are Prime, Pure, Extra No. 1, Crackling Oil, No. 1 and No. 2, Prime being the best. The odor varies from almost none to offensive in the No. 2 samples.

Lard oil is adulterated with cottonseed, corn, and neutral petroleum oils. Cottonseed would be shown by the Halphen test and by the higher Maumené test (sulphuric acid test): should the oil not give the Halphen test, but show a high Maumené value, it is an indication of the presence of corn oil. Neutral petro-

leum would be shown by the flash test and a low Maumené value; ordinary petroleum, by the "bloom" or fluorescence. The oil is used as a screw-cutting oil, for burning (signal oil, miner's lamp oil), for oiling textile material preparatory to spinning, and in soapmaking.

Linseed oil is prepared from flax-seed, which contains about 40 per cent. of oil. The oil receives its name from the locality where the seed is grown, as Calcutta and Western oil. It is of golden yellow color and pleasant odor, and when exposed to the air absorbs oxygen, forming a thin film of a gummy insoluble substance, hence its use as a paint oil. This film is, however, quite porous, and of little protection unless it carries a pigment in it. Linseed oil is thus an example of a drying oil, and it may dry so rapidly as to produce heat and cause fire by spontaneous combustion. Great care should consequently be used to burn up all rags or waste saturated with animal or vegetable oils -particularly linseed - not even saving them for use on the following day. This caution does not apply to mineral oils or mixtures of the above oils with mineral oils where the latter constitute half the volume of the mixture. The oils which are liable to cause spontaneous combustion are, first, the drying oils, as linseed and menhaden; the semi-drying oils as corn, cottonseed, and rapeseed; and also neatsfoot, lard, and red oil

Linseed oil is adulterated with corn, cottonseed, menhaden, and rosin oils, all of which retard the drying tendency. *Neatsfoot oil* is obtained, as its name signifies, from the feet of neat cattle, that is, steers, cows, etc. The hoofs are separated, the bones of the feet disjointed and the latter boiled with water; the emulsion is allowed to settle, and the oil which rises is separated. As is the case with all oils, that which is obtained with the least degree of heat or pressure is the best. It is of light-yellow color, bland taste, peculiar odor, and has little tendency to turn rancid. It is adulterated with fish, rapeseed, cottonseed, and mineral oils: the first three would raise the Maumené figure; the latter, lower it. It is also adulterated with other hoof oils, as sheep-trotter and horsefoot oil, which are difficult of detection. It is used as a lubricant by itself or compounded, and for currying leather.

Rapeseed oil. This oil is obtained from the seeds of plants belonging to the mustard family — turnips and their varieties. The oil is pale yellow to yellow, of peculiar odor and harsh or pungent taste. It is adulterated with cottonseed and refined fish oil: the former would be discovered by the Halphen test; the latter, by the odor. It is used as a lubricant, more particularly in Europe, and as a burning oil.

Rosin oil is obtained by the distillation of common rosin in stills holding about thirty barrels. About 85 per cent. of oil is obtained; this is distilled, redistilled and sometimes distilled again, giving "rosin oil first run," "second run," "third run," and "fourth run." A small quantity of rosin spirits is obtained at the same time. "First run" is employed in making axlegrease, in oiling leather and making cements; "second run" is used in printing-ink and in currying, and the "third" and "fourth runs" are used to adulterate other oils. Rosin oils are thick, reddish-brown, viscous liquids of high specific gravity, 0.981-0.987, and peculiar odor.

Sperm oil. Real sperm oil is obtained from the huge cavity in the head of sperm whales; the term is also applied to the oil obtained by trying out the blubber, as well as to the oil from the Arctic sperm or bottlenose whale. The crude oil, as obtained from the ships, is packed in ice, thus chilling it, is shoveled into bags and pressed after the manner of lard: the solid part, after refining, forms spermaceti, and the liquid portion, sperm oil. It is a limpid oil, of a pale yellow color and faint odor, and is one of the best lubricants we have: of the fatty oils it has the lowest viscosity, and it varies less than that of any other oil with increase of temperature. The common adulterants are whale, mineral and rapeseed oils, also liver oils. Whale oil is indicated by the strong fishy odor and nutty taste, mineral oils by the low flash test corresponding to a gravity of 0.880, and rapeseed oil by the peculiar odor and taste. It is used as a lubricating and (formerly) as a burning oil.

Tallow or ox oil is obtained from beef tallow after the manner of the manufacture of lard oil from lard. It is a light yellow, bland oil, resembling tallow in odor, and is employed in mixing with mineral oils as cylinder oil.

Turpentine is made by the distillation of pine resin or pitch in copper stills of about 800 gallons capacity.

To aid the process, a stream of water is run into the still, making a distillation with steam: the residue in the still is run off into barrels, forming the rosin of commerce. The yield and quality vary according to the length of time the trees have been producing resin, both growing inferior with age. The resin of the first season is called "virgin dip," and produces the finest quality of rosin, "W.W" (water white) or "W.G." (window glass). Other grades are "V," "U," "T," etc., to "A," which is the poorest and blackest.

Turpentine is a colorless liquid of peculiar taste and odor: on exposure to the air it evaporates and partially becomes resinous. It is adulterated with petroleum products — benzine and kerosene — which would be shown by the low flash test and gravity, and by the bloom in the case of kerosene. Wood turpentine, obtained from the distillation of pine stumps and wood with steam, is in many ways a satisfactory substitute for the resin turpentine.

Whale oil is prepared from the blubber of whales after the manner of sperm oil, to which it is similar. It has a strong fishy odor, a nutty taste, and is light yellow to brown in color. A customary adulterant is seal oil, which it is practically impossible to detect. It is used as a leather dressing, as a burning oil, and for lubricating purposes.

Blown oils. Blown, Base, Thickened or Oxidized oil is usually prepared by heating the oil from 160 to 230 deg. F. in a jacketed kettle and forcing a current of air through it: after the action is once started, no further heating is usually necessary. The color of

the oil darkens somewhat, but the specific gravity and viscosity are much increased.

The oils submitted to this process are chiefly rape and cottonseed, making "Lardine," although it is often applied to linseed, sperm, and seal oils. These blown oils are used to mix with other oils to increase their viscosity for lubricating purposes.

Besides these oils the following are of interest:

Clock and Watch oil. This is obtained from the jaw and head of the blackfish or dolphin, also an inferior quality from the blubber. The oil is pressed after the manner of sperm oil, bleached and refined by sunning in contact with plates of lead to remove acid. It is a pale yellow, very fluid oil of peculiar odor: it is the highest in price of any of the lubricating oils, being worth from \$5 to \$15 a gallon according to the supply.

Degras. Properly speaking, this is a fish oil used in currying (Moellon), but now applied to wool grease or to a mixture of wool grease and fatty acid from the soap used in scouring wool. It is made by acidifying the settled washings from wool with sulphuric acid, separating the wool grease and fatty acid as a more or less clotted mass, which is washed, filtered off, and pressed in screw presses heated by steam. Or the wool is extracted with naphtha, after the manner of the extraction of vegetable oils, the naphtha solution strained and the solvent distilled off, leaving pure wool grease. This contains practically no free acids nor sulphuric acid, as does the other, and is a much better product. It is called also "Yorkshire Grease," and in a purified form forms the "lanoline" of the apothecaries.

Moellon is a fish oil, oftentimes "cod," which has been oxidized by being absorbed in leather. Chamois skins are "stuffed" with the fish oil, heaped up, when fermentation sets in; they are then heated in water, and pressed, forming a first-quality product or "French degras," as it is called. A second quality is also obtained.

Neutral oil is a petroleum oil which is free from fluorescence or "bloom," and hence may be used for the adulteration of animal or vegetable oils without its presence being evident.

Screw-cutting oil is a paraffin oil of 27 deg. B. mixed with 25 per cent. of cottonseed oil.

Stainless oils are spindle or loom oils mixed with a percentage of animal oil, as lard or neatsfoot, so that the oil spots can be more readily scoured out of the goods.

General Considerations Regarding Lubricants and Choice of a Suitable Oil

The following considerations will aid in the selection of a suitable lubricating oil:

I. Use the most fluid oil that will stay in place and do the work.

2. The flash-point should not be less than 300 deg. F.

3. The evaporation test should be less than 5 per cent.

4. The best oil is that which possesses the greatest adhesion to metal surfaces and the least cohesion among its own particles. These conditions are fulfilled by

mineral oils, sperm oils, neatsfoot, and lard oil, in the order named.

5. For light pressures and high speed, use mineral oils of 30.5 deg. B., flash-point 360 deg. F., also sperm, olive, or rape.

6. For ordinary machinery, use mineral oil of 25 to 29 deg. B., flash-point 400 to 450 deg. F., lard, whale, neatsfoot, tallow, and heavy vegetable oils.

7. For cylinder oils, use mineral oils of 27 deg. B., flash-point 550 to 600 deg. F. alone, and mixed with small percentages (1 to 7) of animal or vegetable oils as degras, tallow, linseed, cottonseed, and blown rape.

8. For heavy pressure and slowspeed, use lard, tallow, and other greases either by themselves or mixed with graphite and soapstone. Rosin greases, made by partially saponifying rosin oil with quicklime, are also used.

The lubricant should be practically free from acid, or contain at most not more than 0.3 per cent. figured as sulphuric anhydride (SO₃), and must be free from lumps, which would stop up the lubricators. It should, if containing mineral oil, be free from tar and residue insoluble in gasolene. This test is made by mixing five cc. of the oil with 95 cc. of 86 to 88 deg. gasolene and allowed to stand for one hour: a good oil should not show more than 5 per cent. of flocculent or tarry matter settled out. It should contain no "oil-thickener," "soap," "pulp," "gelatin," or similar substance added to increase artificially the viscosity, and should be carefully strained into clean barrels. If the lubricant be compounded, the ingredients should be so mixed as to give a perfectly homogeneous product. ENGINE-ROOM CHEMISTRY

Table VII gives a more definite idea of the constants of oil which are used for certain purposes.

Kind	Gravity,	Flash,	Fire,	Viscosity,
	Deg. B.	Deg. F.	Deg. F.	Seconds
Spindle Loom Engine Gas engine cylinder. Cylinder	30-35 28 27-30 26 23-25 26-28	320-390 360 410 509 525 400-575	475 599 600	58-156-70°F 203-70°F 190-210-70°F 135 at 212°F 125-145 212°F 200-300 212°F

TABLE VII

In case it is desired to follow the subject further, the following books can be recommended:

"Petroleum and Natural Gas," transl. by W. T. Brannt.

"Animal and Vegetable Fats and Oils," transl. by W. T. Brannt.

"Lubrication and Lubricants," Archbutt and Deeley.

"Friction and Lubrication," W. M. Davis.

"A Short Handbook of Oil Analysis," A. H. Gill.

APPENDIX

TABLE VIII

Melting-Points of Various Metals and Salts for Use with the Melting-Point Boxes

And the second	the state of the s	AND DESCRIPTION OF TAXABLE PARTY OF TAXABLE PARTY.
	Deg. C.	Deg. F.
Tin	232	440
Bismuth	268	517
Cadmium	320	608
Lead	326	618
Zinc	419	788
Cadmium chloride	541	1005
Aluminum	657	1150
Potassium bromide	722	1328
Sodium bromide	752	1382
Potassium chloride	800	1472
Sodium carbonate	849	1560
Calcium fluoride	902	1648
Barium chloride	922	1690
Copper	1065	1950

ENGINE-ROOM CHEMISTRY

TABLE IX

Relation of the Centigrade and Fahrenheit Scales

Deg. C.	Deg. F.	Deg. C.	Deg. F.	Deg. C.	Deg. F.
0	32	65	149	160	320
5	41	70	158	170	338
IO	50	75	167	180	356
15	59	80	176	190	374
20	68	85	185	200	392
25	77	90	194	220	428
30	86	95	203	240	464
35	95	100	212	260	500
40	104	110	230	280	536
45	113	120	248 .	300	572
50	122	130	266	320	608
55	131	140	284	340	644
60	140	150	302	360	680

TABLE SHOWING THE COMPARISON OF SPECIFIC GRAVITY WITH BAUMÉ DEGREES

Baumé	Sp. Gr.	Baumé	Sp. Gr.
IO	1.000	29	0.881
12	0.986	30	0.875
14	0.972	35	0.848
16	0.959	40	0.823
18	0.946	45	0.800
20	0.933	50	0.778
21	0.927	55	0.757
. 22	0.921	60	0.737
23	0.915	65	0.718
24	0.909	70	0.700
25	0.903	75	0.683
26	0.897	80	0.666
27	0.892	85	0.651
28	0.886	90	0.636

The specific gravity can in general be found by the formula $\frac{143}{133 + B^{\circ}}$. B° represents the reading Baumé at 60 degrees F.

ENGINE-ROOM CHEMISTRY

TABLE XI

Showing the Specific Gravity, Degrees Baumé, Weight per Gallon and per Cubic Foot of Certain Oils

Oils	Sp.Gr. 60º F.	Degrees B.	Lb. per Gal.	Lb.perCu.Ft.
Castor	0.961	15.66	8.01	60.06
Cottonseed	.922	21.83	7.68	57.62
Horse	.919	22.17	7.66	57.44
Lard	.915	23.00	7.62	57.14
Linseed	.934	19.87	7.79	58.37
Neatsfoot .	.915	23.00	7.62	57.14
Olive	.916	22.80	7.63	57.25
Rape	.916	22.80	7.63	57.25
Sperm	.880	29.00	7.34	55.00
Tallow	.916	22.80	7.63	57.25
Turpentine	.866	31.60	7.22	54.12
Whale	.927	21.00	7.72	57.93
Water	1.000	10.00	8.33	62.50

APPENDIX

TABLE XII

Showing the Viscosity, Flash, Valenta and Maumené Tests of Certain Oils

	Viscosity		Flash	Valenta	Maumené
	Doolittle, grams at 70 deg. F.	Saybolt, seconds at 70 deg. F.	Deg. F.	Deg. C.	Deg. C.
	,	1			
Castor	VISCIO	1321	345	20	47
Colza	see Rape	_		-	-
Cottonseed	82.5	2102	582	90-110	76
Horse	_	_	_	54- 80	52
Lard	82.8	215	530-600	54- 98	41
Linseed	80.0	200 ²	525	57-79	III
Neatsfoot .	83.7	250	440	62- 75	42
Olive	66	682	450	85-111	35
Rape	86.5	350 ²	530	Insoluble	55
Sperm	73.5	102	430-480	Insoluble	46
Tallow	75.0	125 ²	560	71-75	35
Turpentine	—	_	119-125		-

1 At 140 deg. F.

² Calculated from Doolittle reading.





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