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THE ABSORPTION SPECTRA OF CERTAIN SALTS OF COBALT, ERBIUM, NEODYMIUM AND URANIUM, AS AFFECTED BY TEMPERATURE AND BY CHEMICAL REAGENTS.

BY HARRY C. JONES AND W. W. STRONG.

[THIRTY-SECOND COMMUNICATION.]

(The results recorded in this paper are a part of those obtained in an investigation on the absorption spectra of solutions that is being carried out with the aid of a grant from the Carnegie Institution of Washington.[1])

PART I.

Introduction.

The problems connected with the absorption and emission of light are of fundamental theoretical importance, and until they are solved we cannot claim any considerable knowledge concerning the structure of molecular and atomic systems, since light and heat radiations and absorptions are among the most characteristic properties of molecular and atomic structure. Although the conditions under which molecular and atomic systems absorb light are extremely complex and even yet are but partially understood, still many important facts are being discovered which increase our knowledge of molecular, atomic and interatomic structure.

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[1] See Publication No. 130, Carnegie Institution of Washington.

Broadly speaking, the spectra of bodies can be divided into five kinds:

1. The first kind consists of a selective absorption and emission in which one or more ions or electrons for every molecule takes part. Examples of this kind of spectra are those of the organic dyes, and probably of many of the fluorescent and phosphorescent compounds of calcium, barium and strontium that have been investigated by Lenard and Klatt and others. These have been discussed in previous papers.[1]

2. The second kind of spectra consists of selective absorption and emission, which, in some cases, is made up of very fine bands. The vibrators in many cases (as indicated by the Zeeman effect which many of the bands show) seem to consist of electrons. The Zeeman effect is different and considerably more irregular than in the case of spark and arc lines. In some cases the Zeeman effect is of the same sign as that given by a positive electron. Only one electron or ion for every 100 to 10,000 molecules takes part in the absorption. Examples of this kind of spectra are furnished by the praseodymium, neodymium and erbium salts in solution, and possibly also by the uranium and cobalt salts. In some respects the uranium spectra are very different from the others, and as few definite Zeeman effects have been obtained, it may be that the mechanism of the absorption of the uranium salts is quite different from that of erbium and neodymium. A full discussion of this type of spectra will be given in the second part of this paper.

3. The third kind of spectra are the banded spectra of gases. These consist of groups of extremely fine lines. The law of Deslandres holds for the wave-length distribution of these lines and bands throughout the spectrum. For this kind of spectra the number of electrons and the damping factors have not been determined. In the case of the banded spectra of the fluorides and chlorides of calcium, barium and strontium, Dufour has obtained Zeeman effects that indicate the

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[1] Jones and Strong: THIS JOURNAL, **43**, 100 (1910). Strong: Chemical Constitution and the Absorption of Light, THIS JOURNAL, **44**, 85, 107.

possible presence of positive electrons. Wood has succeeded in dividing the complex fluorescent spectra of sodium into simple series of lines, each one of which is stimulated by monochromatic light of a definite wave length.

4. The fourth kind of spectra consists of the emission and absorption spectra of gases, so-called line spectra, for which series formulas are in many cases applicable. The Zeeman effects in many cases indicate the presence of negative electrons and for the normal triplet the mean value of $e/m = 1.775$ has been found. It is possible that one or more electrons, or a system of electrons, in each atom take part in the absorption, although at any one instant only a few atoms in the gas are absorbing or emitting. Stark, Füchtbauer and others believe that these spectra are due to some kind of electrical dissociation.

5. The fifth kind of spectra consists of general emission and seems to be due to metallic electrons—electrons that are more or less free to move between the atoms.

Only the first two kinds of spectra are of interest in the present investigation, and as the second kind will be discussed later, the first type will be considered here. Attention is called to the recent papers of Koenigsberger and Kilchling[1] in this connection.

The absorption and reflection of light by the aniline dyes has been treated by Helmholtz, Drude, Lorentz, Planck, Voigt, and others, in the discussion of their electromagnetic dispersion theories. It is found that the reflecting power for any wave length is greatly affected if an absorption band lies in the neighborhood. In the region of absorption the value of nx (n the refractive index, and x the coefficient of extinction) may range from 0.1 to 6, whereas at distances of 1μ or more from the maximum of absorption it is never greater than $1(10)^{-6}$.

Using the Reiff-Drude formula, Koenigsberger and Kilchling found the following values:

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[1] Ann. Phys., **28**, 889, 925 (1909); **32**, 843, 867 (1910).

	e/m.	
Tetraiodfluorescein	$1.25(10)^7$ negative electrons	Maximum of absorption shifts 8$\mu\mu$ to the red when heated to 77°.
Fuchsine	1.37 negative electrons	Shift, 17$\mu\mu$.
Cyanine	....	Shift, 6$\mu\mu$.

COBALT SALTS.

Review of Previous Work.

Some of the most beautiful color changes known are those shown by solutions of cobalt and copper salts. For example, aqueous solutions of cobalt chloride are purplish red in color. When a concentrated aqueous solution of cobalt chloride is heated, or treated with hydrochloric acid, aluminium chloride, or calcium chloride, its color changes to blue, the change being quite sudden under certain conditions. On the other hand, the addition of zinc and mercury chlorides produces the reverse effect, changing the blue solution into a red one. Similar changes result when cobalt salts dissolved in other solvents are treated in the same way as aqueous solutions. A very considerable amount of work has been done on this subject by various workers and in general different theories have been offered to explain the results.

Russel,[1] Potilitzin,[2] Lescoeur,[3] Étard,[4] and others, favored the view that these color changes were due to the formation of different compounds of the cobalt salt with the solvent. The hexahydrate $CoCl_2.6H_2O$ is red, and when heated it is changed into the reddish lilac dihydrate, $CoCl_2.2H_2O$. When the latter compound is heated it is transformed into the dark violet monohydrate $CoCl_2.H_2O$. The anhydrous salt is blue and is formed at about 140° C. Étard showed that the solubility curve changed in direction at the tempera-

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[1] P. Roy. Soc., **32**, 258 (1881). Chem. News, **59**, 93 (1889).

[2] Bull. soc. chim., [3] **6**, 264 (1891). Ber. d. chem. Ges., **17**, 276 (1884).

[3] Ann. chim. phys., [6] **19**, 547 (1890).

[4] Compt. rend., **113**, 699 (1891).

ture at which the red solution becomes blue. Charpy[1] showed the same to be true for the vapor tension-temperature curve.

Engel,[2] Donnan and Bassett [3] Donnan,[4] Moore,[5] and others do not believe that these color changes are solvation effects at all. Engel considers that double haloid salts may be formed. He points out that the blue anhydrous cobalt chloride becomes red when sufficiently cooled, and that the red anhydrous sulphate becomes violet when heated. Donnan and Bassett consider that the blue color of cobalt salts is due to the formation of complex anions containing cobalt. From boiling-point determinations they concluded that mercuric and cobalt chlorides in solution form compounds. When metallic ions of relatively strong basic properties like the alkaline earths or hydrogen are introduced with chlorine ions into a cobalt chloride solution, there is a formation of complex cobalt anions similar to those represented in the following schemes:

$$CoCl_2 + 2\overline{Cl} \rightleftarrows \overline{CoCl_4} \qquad CoCl_2 + \overline{Cl} \rightleftarrows \overline{CoCl_3}.$$

On the other hand, zinc, cadmium, mercury, antimony, tin, etc., form negative complexes more easily than cobalt, and hence they will cause the cobalt complexes to break up:

$$\overline{CoCl_4} \rightleftarrows CoCl_2 + 2\overline{Cl}, \qquad ZnCl_2 + 2Cl \rightleftarrows \overline{ZnCl_4}.$$

Vaillant[6] has made a quantitative comparison between dissociation and light absorption of certain electrolytes. In general, there is a close parallelism between these two phenomena. For concentrated solutions, however, there are marked differences which suggest the presence of other products than the simple salts and these Vaillant called hydrates. Pflüger[7] and Vaillant and Moore[8] have studied various salt solutions photometrically. They find the same absorption

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[1] Compt. rend., **113**, 794 (1901).

[2] Bull. soc. chim., [3] **5**, 460 (1901).

[3] J. Chem. Soc., **81**, 942 (1902).

[4] Versuche über der Beziehung zwischen der elektrolytischen Dissoziation und der Lichtabsorption in Lösungen. Z. physik. Chem., **19**, 465–488 (1896); **53**, 317–320 (1905).

[5] Physic. Rev., **23**, 321, 357 (1906).

[6] Ann. chim. phys., [7] **28**, 213 (1903).

[7] Ann. Phys., [4] **12**, 1903.

[8] *Loc. cit.*

coefficients for dilute solutions of sodium, potassium, and barium permanganates, but for concentrated solutions they find differences. They conclude that absorption depends upon ionization.

A very detailed study of the effect of temperature on the absorption spectra of solutions has been made by Hartley.[1] He considered that the effect of change in temperature was largely due to change in the solvation of the dissolved salt. Bois and Elias[2] studied cobaltammonium sulphocyanate at 18° and —190° C. At the lower temperature the bands were smaller but were still very diffuse.

Uhler[3] has studied cobalt salts very systematically. Cobalt chloride in water was found to show rather fine bands at λ 6970, λ 6610, λ 6400 (weak), λ 6245 (weak), and λ 6095 (weak). In ethyl alcohol bands were found at λ 6950, λ 6360, λ 6150, and λ 6000.

Jones and Anderson[4] have made a detailed study of cobalt salts. Solutions of all the salts studied, except the sulphate, have a region of ultraviolet one-sided absorption. This they consider as due to association or solvation. In addition to the one-sided ultraviolet band, cobalt chloride has a band at λ 3300 which disappears very rapidly with dilution. This band they believe is due to some simple hydrate, and they consider that this simple hydrate is stable only in very concentrated solutions or at high temperatures. The green band appears for all aqueous solutions, and is independent of whether the cobalt exists as an ion, as a molecule, as an aggregate, or as a solvate, the absorbing power being apparently due to the cobalt atom. Absorption in the red is considered to be due to a simple solvate. In alcohol cobalt chloride has bands at λ 3100 and λ 3600, and also a green band. In methyl alcohol they find a fairly narrow band at λ 5910; one at λ 6050; a narrow intense band at λ 6240; a wide band at λ 6450; and a wide intense band at λ 6700. The position and

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[1] Dub. Trans., [2] **7**, 253, 312 (1900).

[2] Ann. Phys., **12**, 262 (1908).

[3] Hydrates in Aqueous Solution, Carnegie Institution of Washington, Pub. No. 60.

[4] The Absorption Spectra of Solutions, Carnegie Institution of Washington, Pub. No. 110.

relative intensity of these bands are very different from that of the cobalt chloride water bands described by Uhler. In acetone broad bands appear at λ 5725, λ 6200, and λ 6780. These do not appear to be broken up into sharper bands under any conditions. By the addition of 5 per cent. of water to an ethyl alcohol solution of cobalt chloride, the water bands are made to appear, while for an acetone solution it requires the presence of at least 10 per cent. of water to bring out the water bands. Cobalt and calcium bromide in water are found to give bands at λ 6400, λ 6650, and λ 6950. Cobalt bromide in acetone has bands in the red that differ quite markedly from those of cobalt chloride in acetone.

Cobalt chloride in water (Böhlendorf).	Cobalt chloride in alcohol (Böhlendorf).	Cobalt chlorate in alcohol (Formánek).
λ 7100 to 6880	λ 7100 to 6570	λ 6850 to 6320
λ 6750 to 6530	....	....
λ 6400	λ 6400	....
λ 6260 to 6170	λ 6250 to 6170	λ 6245
λ 6070	λ 6070	λ 6058
λ 5610 to 4980	λ	λ 5906
		λ 5720
		λ 5265
		λ 5120

Rizzo[1] has investigated the effect of rise in temperature on the absorption bands of cobalt glass. He gives the following figures:

15°.	300°.	500°.
λ 6870 to λ 6380	λ 6900 to λ 6480	λ 6920 to λ 6460
λ 6030 to λ 5780	λ 6110 to λ 5800	λ 6130 to λ 5800
λ 5520	λ 5630	λ 5650

From the above summary it will be seen that our knowledge of the red cobalt bands is very limited at present. Much more work, similar to that on the uranyl bands described below, remains to be done. Apparently these cobalt bands are somewhat different from the uranyl bands; at any rate, the bands investigated by Bois and Elias did not break up into fine, sharp bands at very low temperatures.

In discussing the various spectrograms that show the effect

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[1] Atti Torino, **26**, 632–638 (1891).

of change in temperature on the absorption spectra of salts, these spectra will be divided into three kinds:

The first kind of absorption consists of wide bands, in many cases hundreds of Angström units wide. In many of the spectrograms only one edge of the band may appear, the other edge of it lying in parts of the spectrum to which the photographic film is not sensitive, or to which the spectroscopic apparatus is not properly adapted. Examples of this kind of absorption are given by the copper or nickel salts, the ferricyanides, the chromates, etc. There is not the slightest indication of a finer structure to these bands.

The second kind of absorption spectra consists of diffuse bands that are quite narrow in many cases, and are usually very weak at ordinary temperatures. These bands may be from 10 to several hundred Angström units wide, and at very low temperatures may be broken up into finer and sharper bands. Examples of this kind of bands are the cobalt, uranyl, or uranous bands. In many cases these bands appear only under very special conditions of concentration and depth of cell. If the amount of absorbing material is large there is usually a wide absorption band in the region. This is well illustrated by the uranyl bands and the blue-violet band of the uranyl salts. If the amount of absorbing material is small the transmission of light is so great that these faint bands are entirely obliterated.

The third class of bands are sharp and appear over rather wide ranges of concentration. They are exemplified by the neodymium and erbium bands. This classification of bands is quite adequate for the present article on account of the salts studied and the temperatures used. It is very probable, however, that the latter two kinds of bands gradually merge into each other.

Glycerol Solutions of Cobalt Salts.

A dilute solution of cobalt chloride was placed in the silica cell and exposures were made at 10°, 100°, and 200° C. At 10° and 100° there was practically complete transmission throughout the visible portion of the spectrum. At 200° the whole shorter wave-length portion of the spectrum was absorbed up to λ 6200. No indications of any fine bands in the red were to be noticed. A solution of normal cobalt bromide in glycerol was exposed in the same way as the chloride. There was practically no change in the absorption with rise in temperature. A more concentrated solution of cobalt bromide in glycerol was exposed in the silica cell at 10°, 100°, and 200°. At 10° there was a very diffuse absorption band extending from λ 5000 to λ 5300. At 100° this band had broadened so as to reach from λ 4900 to λ 5400. At 200° the whole of the spectrum of shorter wave length than λ 6200 was absorbed. No signs of the red bands appeared. Concentrated solutions of cobalt salts in glycerol become blue on being heated. Unfortunately the length of the silica cell prevented the use of concentrated solutions.

Summary.

It was found that glycerol solutions of the cobalt salts investigated do not show any of the fine red cobalt bands. Rise in temperature of the more concentrated solutions caused the yellow absorption band at λ 5100 to widen and to broaden out, so as finally to absorb all the red and thus cause the solution to appear blue.

Concentrated aqueous solutions of cobalt chloride show an enormous increase in the absorption with rise in temperature. Between quite narrow ranges of temperature there is a very great increase in the red absorption in the region of the finer bands. As the concentration is increased the temperature at which this great increase in the absorption takes place is lowered. For the more dilute solutions the widening of the absorption with rise in temperature is quite symmetrical.

The effect of rise in temperature on the absorption of cobalt nitrate and cobalt sulphate is quite small as compared with the effect on the chloride.

The presence of calcium or aluminium chloride with cobalt chloride in water increases the effect of temperature on the absorption, and causes the red absorption to take place in more dilute solutions than it does in pure cobalt chloride solutions. The temperature at which the absorption in the red increases so greatly may be called the "critical color temperature."

The "critical color temperature" seems to depend upon the existence of some *solvate* or *peculiar condition of the cobalt molecule.* The critical color temperature is much higher in water and glycerol than in other solvents. In a similar manner the water and glycerol bands are more persistent than the alcohol or acetone bands. It is important that a complete study be made of the critical color temperature for the various cobalt salts, and for the same salt in different solvents and when mixed with other salts. At the same time a study of the characteristic cobalt bands could be made.

A preliminary test was made to find if the presence of the NO_3 ion and water had the same hypsochromous effect[1] on the cobalt bands as it has on the uranyl bands. Unfortunately, no bands of any strength have as yet been detected for cobalt nitrate in water.

ERBIUM SALTS.

Of all compounds known, those of erbium probably show the most characteristic absorption spectra in the solid state and in solution. The first to make a detailed study of the erbium spectrum was H. Becquerel.[2] One of the minerals that he studied was xenotin or hussakite, a uniaxial crystalline compound consisting mainly of the phosphates of yttrium and erbium. The wave lengths of the ordinary and extraordinary spectrum bands are given. Becquerel found that the absorption spectrum observed in any direction through the crystal was made up by the superposition of two series of bands, one corresponding to vibrations normal to the axis of the crystal and the other to vibrations parallel to this axis.

Schulz[3] has worked on the effect of a magnetic field on the absorption spectrum (obtained by reflection) of erbium oxide. He finds that the bands $\lambda\lambda$ 4482.2, 4491.3, 4510.5, 4541.9, 4554.1, 4562.6, 4571.8, 4579.1, 4606.5, 4625.9, 5197.0, 5205.5, 5242.2, 5261.0, 5387.7, 6430.0, 6476, 6496, 6524, 6538, 6546, 6562, 6581, 6598, 6617 and 6652 broaden when the magnetic field is turned on; λ 4482.2 is shifted to the red; while λ 4510.5 and λ 4562.6 are shifted towards the violet.

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[1] Strong: Physic. Review, **29**, 555 (1909).

[2] Ann. chim. phys., [6] **14**, 194 (1888).

[3] Astrophys. J., **30**, 383 (1909).

Bois and Elias[1] have made a very thorough study of the absorption of hussakite, erbium yttrium sulphate, erbium nitrate and erbium magnesium nitrate at 18° and at —190°, and also of the Zeeman effect at these temperatures. As the results are all collected in the above reference no detailed account is given here. In general, the bands show a Zeeman effect. Doublets and triplets are quite common.

A very extended investigation of the effect of low temperatures and magnetic fields on the absorption spectra of erbium has been made by J. Becquerel. As his papers are somewhat scattered, we give a rather full account of them. His first work[2] was upon the effect of a magnetic field on the absorption spectra of xenotin and tysonite at ordinary temperatures. In the following table + signifies a strong band and + + a very strong band. Field always refers to the magnetic field which in this work is usually 14,100 c.g.s. units. Wave lengths are given in Angström units.

When the optic axis is parallel to the beam of light a crystal behaves like an isotropic body. When placed in a magnetic field, however, a rectilinear vibration is transformed into an elliptical one. This is Becquerel's magnetic double refraction. The effect of the magnetic field on vibrations normal to the field is different from the effect on vibrations parallel to the field. A crystal less than 1 mm. thick in a field of 2720 c.g.s. units causes a difference of $^1/_3\lambda$ in the middle of some bands.

To explain the Zeeman effect observed we must consider whether the external field is simply added to the intramolecular fields or whether there are variations produced there by the presence of the atoms. If we assume the same vibrators in every case, electrons with a value e/m of $1.8(10)^7$, then the internal magnetic fields must vary between 200,000 c.g.s. units in one direction and about the same number of units in the opposite direction. Assuming, on the other hand, that the external magnetic field is simply added to the intra-

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[1] Ann. Phys., **27**, 279 (1908).

[2] Compt. rend., Mar. 26, Apr. 21, May 21, Nov. 19, Dec. 3, Dec. 10, Dec. 24, 1906; Jan. 21, 1907. Le Radium, Feb., 1907.

Xenotin.

Wave lengths.		I. Optic axis parallel to field.		II. Optic axis parallel to light beam.		III. Optic axis normal to field and light beam.[1]
Ordinary spectra.	Extraordinary spectra.	(*a*) Ordinary vibrations normal to the field.	(*b*) Extraordinary vibrations.	(*c*) Ordinary vibrations normal to the field.	(*d*) Ordinary vibrations parallel to the field.	(*e*) Extraordinary vibrations normal to the field.
5206.5++	......	Doubles sym.		Doubles dis. sym. 3.1 A. U.	Spreads towards violet	
	5206.7++		Broadens unsym.			Doubles 3.7 unsym.
5211.3++	......	Broadens sym.		Doubles	Broadens	
5215.5++	......	Broadens sym.		Displaced to red	Doubles 3.7	
	5220.1++		Broadens unsym.			Broadens to red
5221.5++	......	Doubles 5.9 sym.	Displaced 1.0 to violet	Displaced to violet		
5225.6	......	Doubles 5.1 sym.		Displaced 1.0 to violet	Displaced to violet	
5236.6++	......	Broadens sym.		Broadens	Doubles symmetrically	
	5237.2++		Broadens			Broadens
5242.0++	......	Broadens sym.		Broadens	Broadens	
5245.8+	......	Broadens		Doubles unsym.	Broadens	
5251.1	5251.1++	Doubles 2.6	Broadens	Doubles unsym.		Doubles unsym.
	5268.0+		Broadens			
	5388++ 5394++ }		Doubles unsym.			Spread out towards violet
6422.7	......	Doubles 8.9		No change		
	6424.6++		Broadens			
6434.5	......	Doubles 7.7		No change		
	6435.8++		Doubles 9.8 unsym.			
	6463		Doubles unsym.			Broadens
6505.6+	6504.5	Doubles sym.		Doubles 3.8 unsym.	Spread towards violet	
6523.4++	6528.2	Doubles sym.		Doubles 4.4 unsym.	Spread 3.0 toward violet	
6537.0+	6538.0			Displaced 2.0 to red	Doubles 6.6 unsym.	Displaced to violet
	6542.8++		Doubles 4.7 sym.			Displaced to violet
6542.5	......					
	6563		Displaced to violet			Broadens
	......	Doubles 4.4 sym.		Doubles 4.6 unsym.		
6564.4+	6573.0++		Doubles 4.3 sym.			Spread out towards red
6571.6	......	Displaced 1.7 to red			Displaced to violet	
6581.0+	......	Broadens sym.		Weakened.	Spread out to violet.	

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[1] Ordinary vibrations parallel to the field are the same as those under II*d*.

atomic field, Becquerel gives the following values of $e/m = 2\pi V \frac{d\lambda}{\lambda^2} \frac{1}{H}$, + referring to a positive electron:

	e/m.		e/m.
λ 5206.5^{++}	$+4.5(10)^7$	λ 5211.3^{++}	$-0.3(10)^7$
λ 5215.5^{++}	$+2.1(10)^7$	λ 5221.5^{++}	$+1.6(10)^8$
λ 5225.6	$-1.4(10)^8$	λ 5236.6^{++}	$+2.9(10)^7$
λ 5242.0^{++}	$+1.9(10)^7$	λ 5245.8^{++}	$+4.5(10)^7$
λ 5251.1	$-7.1(10)^7$	λ 6422.7	$-1.6(10)^8$
λ 6434.5	$-1.4(10)^8$	λ 6474.0	$+3.8(10)^7$
λ 6505.6^{+}	$+5.1(10)^7$	λ 6523.4^{++}	$-5.9(10)^7$
λ 6537.0^{+}	$-2.8(10)^7$	λ 6542.5	$+3.4(10)^7$
λ 6564.4^{+}	$-8.6(10)^7$	λ 6581.0^{+}	$+3.6(10)^7$

For convenience we will consider that some of the above bands are due to positive electrons, and some due to negative electrons, according to the value of e/m as calculated from the above formula.

The magnetic rotatory polarization is very closely related to the Zeeman effect, the positive and negative electrons behaving differently in this case also, the sense of the rotation being different for the positive and the negative electrons.

J. Becquerel[1] gives a theory explaining the magnetic optical effects which are observed in crystals. The general basis of his theory is somewhat similar to that of Voigt.[2] The electrons are considered to move along each coördinate axis independently. The three directions are considered to be the same for each electron and independent of the period of the exciting light. The form of the equations is then similar to those of a pendulum experiencing great frictional resistance. The theory as here developed explains some, but not all, of the different types of resolution found experimentally. As different results have been obtained, especially by Page,[3] the development given by Becquerel will not be considered in detail.

Later papers by Becqurel[4] deal with the effect of a magnetic field on the absorption spectra of certain crystals of

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[1] Le Radium, March, 1907.

[2] Ann. Phys., **6**, 346 (1899); **6**, 784 (1901); **8**, 872 (1902).

[3] Trans. Camb. Phil. Soc., **20**, 291, 322.

[4] Compt. rend., Feb. 25, Mar. 25, May 13, June 17, Aug. 19, 1907. Le Radium; Sept., 1907.

xenotin, tysonite, parisite, monazite, apatite, and zircon at low temperatures. The bands in general are displaced towards the violet, especially for tysonite, as the temperature is lowered. Many changes of relative intensity occur and at low temperature the bands are invariably narrower and more intense.

For xenotin the following table is given:

Ordinary spectra.		Extraordinary spectra.	
λ at 25°.	Displacement between 25° and —188°.	λ at 25°.	Displacement between 25° and —188°.
5206.5	Doubled, 0.4 to violet	5206.7	0.4 to violet
5211.3	1.5 to violet	5220.1	1.5 to violet
5215.5	0.5 to violet		
5221.6	0.1 to violet		
5236.6	0.5 to red	5237.2	0.5 to red
5242.0	0.9 to red	5251.1	0.6 to red
5245.8	0.5 to red		
5251.1	0.6 to red	5268	0.4 to violet.

There does not seem to be any relation between the Zeeman effect and the effect due to change in temperature. Becquerel also states that the Zeeman effect is independent of the temperature. Related bands are usually affected in the same way by change in temperature.

The ordinary equation of an electron considered in the theory of dispersion is:

$$m\ddot{x} + \kappa\ddot{x} + n^2x = eE \cos pt.$$

The resistance $\kappa\ddot{x}$ designates a mean resistance, and causes the decay of the light vibration. It may result from sudden shocks undergone in any irregular or fortuitous manner by any of the electrons taking part in the absorption of light. The greater κ is the wider the band will be. The above equation leads to a value of the refractive index μ:

$$\mu^2(1—\kappa^2) = 1 + \Sigma \frac{e_h\partial^2(\partial^2—\partial_{0h}^2)}{(\partial^2—\partial_{0h}^2) + \partial^{2}\partial_h^{\prime 2}},$$

where κ is the coefficient of absorption; $2\pi\partial_{0h}$ is the period corresponding to the middle of an absorption band h; e_h is a coefficient depending on the substance and the band, $e_h = \frac{4\pi V^2e^2/N_h\partial_{0h}^2}{m_h}$; N_h is the number of electrons h/cc.; $\partial_h^1 =$

$\frac{\kappa_h}{m_h}\partial^2_{0h}$. Becquerel has obtained the value of the ratio of ∂^1 at 20° and at —186°. The bands are those of tysonite:

λ at 20°.	Ratio of ′.
4791 spec. extraord.	1.83
5176 spec. ord.	1.84
5235 spec. ord.	1.83
5825 spec. ord.	1.85

The ratios of ∂' are very nearly the same as the ratios of the square roots of the absolute temperature. The width of the bands measured between the maxima of the deviations of the dispersion curve vary directly as the square root of the absolute temperature.

If this law is true, then the size of the bands is proportional to the mean speed of translation of the molecules. Schönrock[1] has shown that the width of bands in a gas results not only from the Döppler effect due to the kinetic motion of the gas molecules, but also from collisions. Collisions determine the sudden and fortuitous variations in the phase, amplitude, and direction of motion of the electrons, and prevent the light that is being emitted or absorbed from being homogeneous. The size of the bands is then a function of the mean length of the wave trains emitted between collisions. If δ is the width of the band between the positions where the intensity of light is half the maximum, and r is the length of the train of waves emitted between collisions, then

$$\partial = \frac{1.39\lambda_0^2}{\pi r} = \frac{1.39\lambda_0^2 u}{\pi v L} = A\frac{\lambda_0^2}{L}\sqrt{\frac{T}{M}},$$

where u is the mean period of translation, L the mean free path, v the velocity of light, A is a constant, M the molecular weight, T the absolute temperature, $L = l_2/\rho^2\sqrt{2\pi}$, l is the mean distance between the centers of molecules, ρ is the distance between two molecules at the time of their collision.

If the temperature of the same mass and volume of a vapor is raised, l and ρ are but slightly changed, so that the width of the bands should vary as the square root of the absolute temperature. The above theory applies to a gas. The width

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[1] Ann. Phys., **20**, 995 (1906); **22**, 210 (1907).

of the bands of solids cannot be explained on the Döppler-Fizean principle, but may be due to the extremely numerous shocks of the molecules. The fineness of the erbium bands may then be due to the union of several atoms into big molecules having a very small velocity of translation. If the molecules are large the collisions will be less numerous.

In a later paper Becquerel[1] gives some values for the terms which appear in his equation for determining the refractive index. It should be stated here that dispersion equations differ considerably according to the assumptions made in their calculation.

Tysonite.

λ at 25°.	*lh* at 25°.	*lh* at —188°.
4791	$2.29(10)^{-7}$	$7.23(10)^{-7}$
5176	$2.14(10)^{-7}$	$5.31(10)^{-7}$
5235	$0.71(10)^{-7}$	$1.53(19)^{-7}$
5825	$4.82(10)^{-7}$	$2.35(10)^{-7}$

From the changes of *lh*, the dielectric coefficient, with changes in temperature, Becquerel considers that the increase in intensity of the bands when the temperature is lowered is not only due to a narrowing of the bands, but also to an increase in the total amount of energy absorbed as the dielectric constant is increased. Let us assume that $e = 3.4(10)^{-10}$.

Tysonite.

	λ 5176.	λ 5235.
e/m	$+2.49(10)^{7}$	$-2.48(10)^{7}$
Ne at 25° U. E. M.	$1.01(10)^{-5}$	$3.28(10)^{-6}$
Ne at —188°	$2.50(10)^{-5}$	$7.07(10)^{-6}$
Nm at 25°	$4.05(10)^{-13}$	$1.32(10)^{-13}$
Nm at —188°	$1.00(10)^{-12}$	$2.85(10)^{-13}$
N at 25°	$0.89(10)^{15}$	$2.9\ (10)^{14}$
N at —188°	$2.21(10)^{15}$	$6.25(10)^{14}$

From the above, then, N, the number of absorbing electrons, increases as the temperature is lowered. The number of absorbing electrons is very much smaller than the number of atoms present. Hallo[2] and others have shown that only a small number of sodium atoms take part in the absorption of the two D lines:

[1] Le Radium, Nov., 1907.

[2] Arch. Néerlandaises, [2] **10**, 148 (1905).

D_2 (Hallo)	$e_{o_2} = 7.5\ (10)^{-8}$	$N_{o_2} = 3.3\ (10)^{14}$
D_1 (Gerst)	$e_{o_1} = 2.1\ (10)^{-7}$	$N_{o_1} = 1.1\ (10)^{15}$
λ 5221.5 (Xenotin)	$e_{25^\circ} = 5.43(10)^{-8}$	$N_{25^\circ} = 3.34(10)^{13}$
	$e_{-188^\circ} = 9.68(10)^{-8}$	$N_{-188^\circ} = 5.96(10)^{13}$

The index of refraction of solids, and especially minerals, changes very little with change in temperature, so that the electrons influencing refraction are but slightly affected by changes in temperature. Drude, Chéneveau,[1] and others, have shown that the number of these electrons vibrating in the ultraviolet is approximately that of the valencies of the atoms composing the molecule.

Becquerel[2] has continued his investigations at low temperatures, doing part of the work with Onnes[3] at Leyden. One of the problems arising from Becquerel's work is whether the paramagnetism of erbium and neodymium affects the internal magnetic fields which would exist within the crystals if they were diamagnetic. For this reason the Zeeman effect is found at widely different temperatures. If the Zeeman effect is independent of temperature then we should consider that paramagnetism did not play a very important rôle. Becquerel finds the Zeeman effect on the bands of xenotin and tysonite to be independent of the temperature.

In a table giving the Zeeman effect for tysonite and parisite it is seen that bands that are in practically the same portion of the spectrum are affected in a very different way by the magnetic field. From the Zeeman effect it is seen that the erbium alcohol bands λ 4870, λ 4880 and λ 5410 are due to negative, λ 5238 to positive electrons.

Considerable data are given by Becquerel upon the rotatory magnetic polarization. The results confirm the theory of the Hall effect—that the sense of the dispersion is just the opposite on the outside of the band to what it is on the inside. Applying the theory to the band λ 5221.5 of xenotin, Becquerel obtains the results shown in the following table:

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[1] Le Radium, June, 1907.

[2] *Ibid.*, Jan., 1908; Nov., 1909. Compt. rend., Dec. 9, 30, 1907.

[3] *Ibid.*, Aug., 1908.

Temperature	H.	e/m.	N_e.	N_m.	N.
20°	14,100	$1.656(10)^8$	$3.78(10)^{-7}$	$2.28(10)^{-15}$	$3.34(10)^{13}$
—188°	12,300	$1.656(10)^8$	$6.74(10)^{-7}$	$4.07(10)^{-15}$	$5.96(10)^{13}$

Erbium Chloride in Glycerol.

Several photographs were made of the absorption spectra of erbium chloride dissolved in glycerol. The absorption is very similar to that of an aqueous solution, the bands, however, in general being shifted towards the red. The bands shown by a solution 30 mm. in depth are located as follows: λ 3250; λ 3370; λ 3510. These three bands are quite strong, being some 30 or 40 Angström units wide; λ 3600 is weak and narrow; λ 3650 is quite strong; λ 3785 is quite strong; λ 3885 is considerably weaker than the five other ultraviolet bands described above; λ 4165, λ 4490 and λ 4520 are of about equal intensity and quite strong (in the region near these bands there are numerous weak bands and these would come out better if a greater depth of cell could have been used, but on account of the slight solubility of erbium chloride in glycerol the use of a greater cell depth was not practicable); λ 4910 weak; λ 5190; λ 5210; λ 5225 rather strong; λ 5240 weak; λ 5260 weak; λ 5380; λ 5420; λ 5440; λ 6450; and λ 6530. The measurements were from a spark line at λ 3995 and hence are more accurate in this region. On the whole, most of the erbium chloride bands are of greater wave length for the glycerol solution than for the aqueous solution.

The relative intensities of the water and glycerol bands differ considerably, but the wave lengths do not appear to be very greatly changed. The photographic films appear to have contracted differently on drying, so that no very accurate comparisons of the wave lengths of the water and glycerol bands could be made.

Rise in temperature from 15° to 200° produces no noticeable change in wave length. At the higher temperature the bands are very much less distinct and apparently considerably weaker. For instance, the group of bands at λ 5200 at 15° practically becomes a single hazy band at 200°.

Absorption Spectra of Erbium Nitrate and Other Salts of Erbium.

It was thought to be of interest to test whether the NO_3 group had any hypsochromous effect on the absorption spectra of aqueous solutions of erbium salts. The following approximate wave lengths of the bands do not show any such hypsochromous effect as was found for the uranyl bands:

Erbium. nitrate.	Erbium chloride.	Erbium nitrate.	Erbium chloride.	Erbium nitrate.	Erbium. chloride.
3630	3635	4270[3]		5210	5205
3760[1]		4425	4415	5235	5230
3788[2]	3785	4480[4]		5363	5365
3880[3]		4500	4905	5420	5415
4045		4675[4]	4670[4]	6400	6410
4000		4730[4]		6480	6490
4160	4150	4850	4845	6530	6535
4100		4870	4865		
4215	4210	4910[4]	4905		

The crystals of erbium sulphate have fine absorption spectra. As the water of crystallization is driven off the bands change very considerably and become much more diffuse. The reflection spectra from fused erbium oxide consist of a large number of fine lines. As shown by Anderson, these lines become wider as the temperature is raised, until they become emission bands. The emission bands are quite broad. Between 100° and 600° some of the fine erbium bands shift about 10 Angström units. The difference between the wave lengths of the emission bands and the absorption bands at high temperatures, if it exists at all, is hidden by the haziness of the bands.

NEODYMIUM SALTS.

Introduction.

J. Becquerel has carried out investigations on several neodymium compounds similar to those on erbium. Tysonite was especially studied. This is a fluoride of cerium, lanthanum, and didymium and gives mainly the didymium spectrum. The bands $\lambda\lambda$ 5176++, 5234++, 6250 (doubles 4.5 unsym.),

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[1] Hazy.

[2] Strong.

[3] Wide and weak.

[4] Weak.

6740, 6742+, and 6760+ were found to broaden in the magnetic field. Employing the usual theory of the Zeeman effect, Becquerel shows that λ 3995 is due to positive, λ 5075+ to positive, λ 5109+ to negative, λ 5176++ to positive, λ 5234++ to negative, and λ 7642+ to negative electrons.

At —180° the bands are much finer. The band λ 6249.7 is very fine and from the Zeeman effect it appears to be due to positive and negative electrons. The following table gives some of Becquerel's results.

The series of acetate bands is very much like that of the uranyl series, except that it runs in the opposite direction. The absorption spectra of uranous bromide in glycerol and in methyl alcohol are also similar.

Tysonite.			Parisite.		
λ at —188°.	$\Delta\lambda H = 15000$.	$e/m = 2\pi v \frac{\Delta\lambda}{\lambda^2 H}$.	λ at —188°.	Δλ.	e/m.
3996 s	0.8	$+6.3\,(10)^7$	4274.8 *f*	0.20	$-1.38(10)^7$
4259.8 s and f	0.1	$-0.7\,(10)^7$	4724.7 *f*	0.42	$+2.37(10)^7$
4268 s and f	0.1	$+0.7\,(10)^7$	4747.0	0.40	$-2.20(10)^7$
4721.4 s and f	0.1	$-0.6\,(10)^7$	5095.7 *s*	2.39	$+11.56(10)^7$
5064.4 f	0.4	$+2.0\,(10)^7$	5186.0 *s*	0.37	$+1.73(10)^7$
5073.5 f	0.1	$+5.32(10)^7$	5208.0 *s*	0.37	$-1.71(10)^7$
5079.1 f	0.54	$-2.63(10)^7$	5220.0 *s*	0.18	$+0.83(10)^7$
5087.2 f	0.99	$-4.81(10)^7$	5231.0 *s*	0.27	$+1.24(10)^7$
5098	0.33	$+1.0\,(10)^7$	5256.0	0.60	$-2.70(10)^7$
5110	0.92	$-4.4\,(10)^7$	5685.0	1.00	$+3.90(10)^7$
5173 *s*	0.53	$+2.5\,(10)^7$	6232.7	0.77	$-2.40(10)^7$
5185.7 s and f	0.27	$+1.26(10)^7$	6239.6	1.14	$-3.70(10)^7$
5220 s and f	0.14	$-0.64(10)^7$	6246.9	0.60	$-1.90(10)^7$
5234.6 s and f	0.54	$-2.48(10)^7$	6723.0	0.90	$-2.50(10)^7$
6224.9 f	0.4	$+1.2\,(10)^7$	6735.0	0.90	$-2.50(10)^7$
6234.8 f	0.5	$-1.6\,(10)^7$	6746.0	0.90	$-2.50(10)^7$
6242.6 f	1.2	$-3.90(10)^7$			
6249.7 s and f	3.27	$\pm 10.52(10)^7$			
6267 f	0.4	$+1.30(10)^7$			
6683	1.86	$-5.23(10)^7$			
6740	0.86	$-2.38(10)^7$			
6761	0.41	$-1.13(10)^7$			

The above table shows that the Zeeman effect on related bands of tysonite and parisite is very different (parisite is a carbonate of the didymium group). An examination was made of yellow Spanish apatite, a fluorphosphate of calcium and didymium. The apatite bands are quite broad. The band λ 5270 gave a circular vibration indicating positive, λ 5750 positive, λ 5820 positive, and λ 5860 negative electrons.

A solution of neodymium nitrate in ethyl alcohol has also been tried. The bands λλ 5229, 5219, and 5239 were broken into two components by the magnetic field, the amount being 0.5 Angström unit for $H = 14{,}000$ c.g.s. units. The sense of the polarization indicated negative electrons. The bands λλ 5815 and 5831 are affected but little and indicate positive electrons. The effect of the magnetic field seems to be independent of the solvent. The addition of perchloride of iron had no effect. The spectrum was observed as the solution was warmed so as to change the solid alcohol to liquid alcohol. No discontinuous change in the spectrum was noticed.

Neodymium chloride in alcohol (methyl) has a sensitive band at λ 5096, giving a separation of 1.1 Angström units for $H = 14{,}000$. The sense indicates a positive electron. The band λ 5207 gives a separation of 0.4 having a negative sense, λ 5220 a separation of 0.4 in a negative sense, while λ 5225 does not show any effect. The bands λλ 5761 (0.4, positive), 5787 (0.4, negative), 5796 (negative), and the two bands at 6800 (negative electrons) gave measurable Zeeman effects. No difference was found between "water" and "alcohol" bands.

The addition of small amounts of the nitrate of neodymium to the chloride in an alcoholic solution rapidly causes the disappearance of the bands λλ 5207, 5225, 5727, 5745, and 5761. When equal amounts of the two salts are present these bands have practically disappeared. The band λ 5220 remains. At the same time new bands appear at λλ 5235, 5777, 5814, and 6229. The band λ 5229 is due to negative, λ 5235 to negative, and λ 5814 to positive electrons.

Becquerel and Onnes[1] continued the work on absorption spectra at temperatures of liquid and solid hydrogen. The general effect of cooling is to make the bands more intense and often to cause new bands to appear. The reverse action

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[1] Le Radium, Aug., 1908.

very seldom occurs. But when the temperatures of liquid hydrogen (20° absolute) or solid hydrogen (14° absolute)

	Stahl.	Demarçay.[1]	Muthmann.[2]	Drossbach.[3]	Foesling.[4]	Formánek.[5]	Exner.[6]
A	7420	7324	....	....	....	7291	....
B	6900	6910	6892	....	6895	6906	....
	6810	6804	6798	....	6775	6794	6750
	6710	6731	6720	....	6720	....	....
C	6360	6373	6360	....	6360	....	....
	6280	6292	6285	....	6278	....	....
	6240	....	6250	....	6254	6235	....
	6220	6234	6215	....	6217	....	....
D	....	....	5834	....	....	....	....
	....	....	5808	....	....	....	....
	5790	5783	5785	5880–5660	5788–5780	5797	5795
	5750	....	5754	....	5754	5759	5740
	....	....	5735	....	5735	....	....
	5720	....	5716	....	5716	....	....
E	5330	5320	5323	5320	5323	5319	5235
	5240	....	5254	5270–5190	....	....	....
	5210	5220	5216	....	5216	5222	....
	....	....	5205	....	5204	5209	....
	....	....	....	5160	....	....	5120
	5130	....	5120–5110	....	5124	5120	....
	5090	5109	5089	....	5087	5096	....

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[1] Compt. rend., **126,** 1039 (1898).

[2] Ber. d. chem. Ges., **32,** (1899).

[3] *Ibid.*, **35,** 486 (1909).

[4] Z. anorg. Chem., **118** (1907).

[5] Die qualitat. Spectralanal. anorg. Körper, Berlin (1900).

[6] Sitzun. Wien., **118,** A, 1252–1266 (1899).

are reached it is found that many bands have weakened, or even disappeared. The band λ 5235 of tysonite is a band of this kind. At very low temperatures, then, the spectrum is much simpler than at higher temperatures. Some of the bands even pass through a minimum of width. The band

Table—(Continued).

	Stahl.	Demarçay[1].	Muthmann.[2]	Drossbach.[3]	Foesling.[4]	Formánek[5].	Exner.[6]
F	....	....	....	4780	4799	4821	4830
	4760	4768	4745	....	4748–4742	4759	4760
	4690	4691	....	4710	4687	4695	4700
	4620	4624	4595	4630	4610	4614	4620
G	....	....	....	....	....	4443	4430
	4340	4351	4340	4340	4330	4341	....
	4280	4294	4325	....	....	....	4270
	....	4281	4273	4275	4271	4271	....
	4190	4200	....	....	....	....	....
J	3800	....	3803	....	3804	....	....
K	3560	....	....	3590	....	....	....
	3540	....	....	3560	3538	....	3478
	3500	....	....	3510	3503	....	....
	3470	....	....	....	3468	....	....
L	....	....	....	....	3420	....	....
	3290	....	....	3370	....	....	....
	....	....	....	....	....	....	3350–3130
M	3290	....	....	3280	....	....	....

λ 5176 of tysonite passes through a minimum between 20° and 14°. Becquerel suggests that there should be a relation between the effect of temperature on the absorption and on electrical resistance.[1] At very low temperatures the metals should be transparent.

The effect of a magnetic field on the absorption bands was found to be independent of the temperature, and this fact, Becquerel believes, is a strong argument for the view that positive electrons exist within the atoms.

The foregoing table gives the wave lengths of the neodymium bands in aqueous solution as measured by various spectroscopists:

Stahl states that the bands λ 6950, λ 6840, and λ 6780 vary enormously in their relative intensities in the various solutions. In the presence of strong nitric acid the bands λ 4710, λ 4690, and λ 4750 disappear completely. The absorption spectrum of the chloride is independent of the presence of free acid.

Neodymium: λ 6710, λ 6240, λ 5790, λ 5720, λ 4340, λ 4190, λ 3800, λ 3390, λ 3270.

Praseodymium: λ 5970, λ 5890, λ 4820, λ 4690, λ 4440.

The λ 4690 band is common to solutions of both neodymium and praseodymium, and this had led some to believe that there is a common element in these two substances. Stahl considers the view that there are several elements in neodymium as very improbable.

Neodymium Salts in Glycerol.

A run was made to test whether Beer's law holds for glycerol solutions. A spectrum was taken ranging from 0.84 to 0.105 normal, the amount of absorbing matter being kept constant. The more dilute solutions show greater general absorption in the ultraviolet. Otherwise Beer's law is found to hold.

Plate I, *A*, is the spectrogram of a solution of neodymium chloride in glycerol taken in the silica cell at various temperatures. The plate shows a slight widening of the bands, but this is very small. Some of the finer bands indicate a slight

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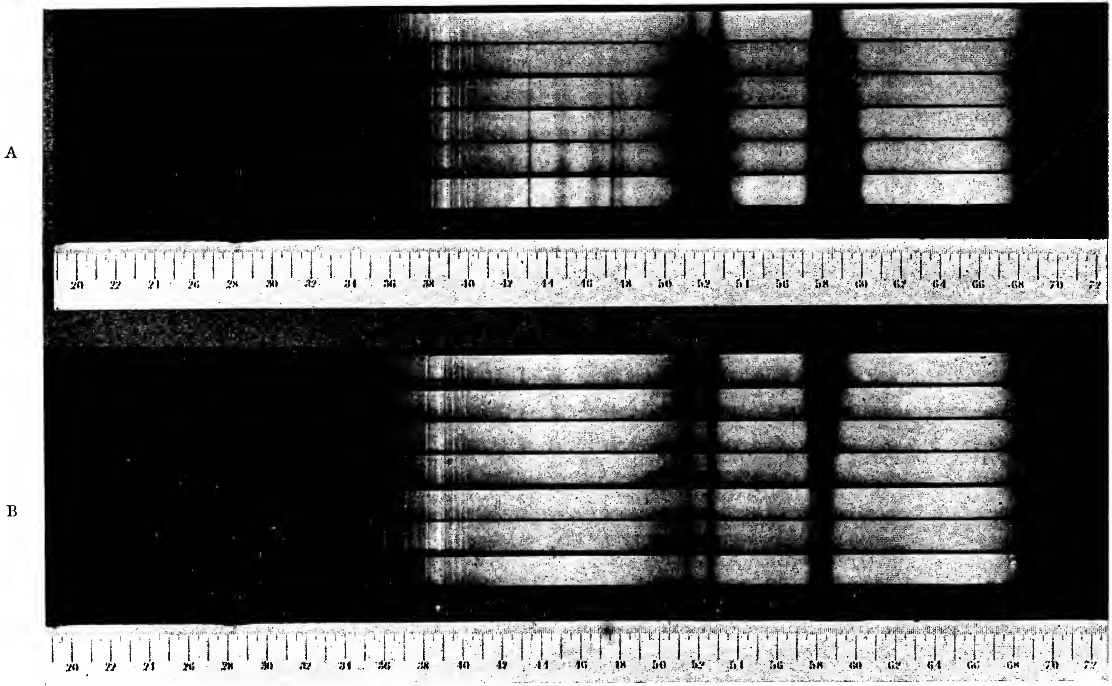
[1] Onnes: Comm. Leyden, Suppl., **9**, 25 (1904); Onnes and Clay: Comm. Leyden, **95**, 99.

Plate I.



shift towards the red with rise in temperature. This, however, is quite small and never amounts to more than 3 or 4 Angström units for any band.

A plate was made showing the effect of rise in temperature of solutions containing neodymium and aluminium or calcium chlorides in glycerol. In the third and fourth strips it is to be noticed that the wide band at λ 5800 is shifted slightly to the red. The band at about λ 4295 seems to be shifted 2 or 3 Angström units to the red. The shift is very small and is obscured in part by the increased diffuseness of the bands at the higher temperature.

The effect of rise in temperature on the absorption spectra of pure neodymium chloride in glycerol was studied. The shift of the bands in this case can hardly be noticed. The effect of the presence of calcium chloride is to cause the temperature shift of the bands to be increased. The effect is not as great as it is in aqueous solutions.

The absorption spectrum of neodymium chloride (Plate I, *A* and *B*) in glycerol is very similar to that of an aqueous solution. The ultraviolet bands $\lambda\lambda$ 3475 and 3550 are quite strong and sharp. A weak band appears at λ 3520. For the 3 mm. depth of cell and smallest concentration the following bands appear: $\lambda\lambda$ 4290 (weak), 4710 (very weak), 5120 (wide, hazy, and apparently a triplet), 5230, 5240 (strong and fairly sharp), 5250, 5270 (weak and fuzzy), 5740 (wide and hazy), 5790, 5805, 5820 and 5850. The latter three bands practically merge into a single band, the transmission between them being very weak.

The greatest concentration of the 9 mm. depth of cell (upper strip of Plate I, *A*) shows several additional bands: $\lambda\lambda$ 3600, 4190 (very diffuse), 4288 and two very fine components at 4270 and 4305, 4330, 4345, 4365, a wide (50 Angström units) band at 4460, and similar but weaker bands at 4620, 4840, 5340, 5940, 6240, 6265, 6400, 6800, with narrower and sharper bands at 4710, 4730, 4760, 4790, 5170, and 5190.

The "glycerol" bands are very similar to the "water" bands but are all of slightly greater wave lengths. The sharp "water" band at λ 4274 is composed of three bands in the glycerol solution. The "glycerol" bands are quite persistent and for a solution containing 10 per cent. water the bands are practically "glycerol" bands. In general, the "water" and "glycerol" bands are so close to one another that we can not tell whether both bands coexist when the neodymium salt is dissolved in a mixture of the solvents. But the λ 4288 band apparently shifts gradually into the λ 4274 "water" band. No sign of the two bands coexisting is to be seen.[1]

Neodymium Nitrate in Nitric Acid.

Plate IV, *B*, shows the absorption spectra of neodymium nitrate in nitric acid. The effect of free nitric acid is very pronounced. All the bands are wide and diffuse and differ very much from the absorption when there is no free acid. The first band to appear is λ 5830 and shows as a very faint diffuse band. Then come the bands λλ 3470, 3520, 3550, 5130, 5250, 5730, 5970, and for a greater depth of cell λλ 4280, 4310, 4340, 4360, 4390 to 4460, 4480, 4600, 4650 (weak), 4705 (strong), 4745 (strong), 4840, 5385 (strong), 6245, 6275 and 6770.

In general, it has been shown that the effect of nitric acid is to shift the uranyl and uranous bands to the violet. This does not seem to be the effect of adding a large amount of acid to neodymium nitrate in aqueous solution. Many of the above bands do not seem to be bodily shifted to the red, but, like the band marked λ 4280, they are widened on the red side. The narrow band λ 4274 of the neutral nitrate lies within the broad and diffuse band λ 4280. As will be remembered, free nitric acid caused the uranyl nitrate bands to become sharper. At the same time the bands were shifted to the violet.

Some of the bands that Stahl considered as absent in the presence of nitric acid appear on our plates, the band 4705 above apparently being the same as his bands λλ 4690 and 4710.

Spectrophotography of Chemical Reactions.

During the progress of the work quite a number of photographs were made of a salt in mixtures of two solvents. It

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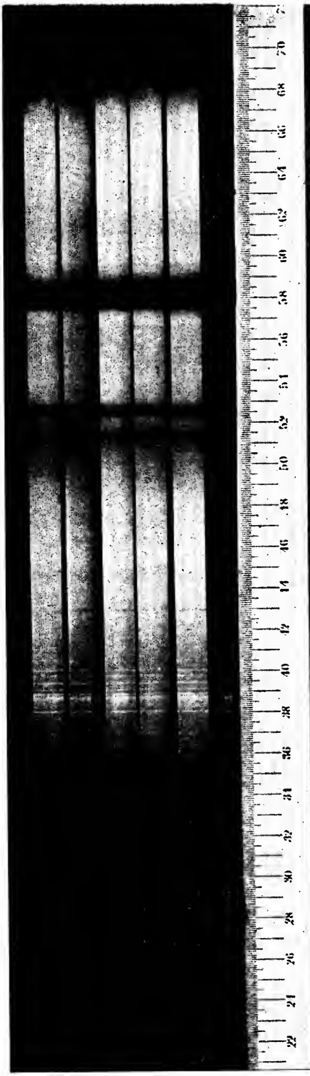
[1] For a detailed description of any plates not described in full in this paper see Publication 130 of the Carnegie Institution of Washington.

Plate II.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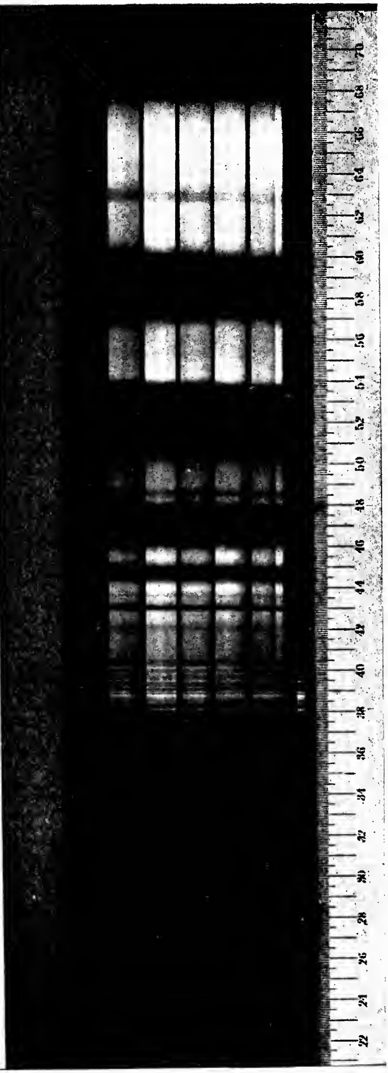
A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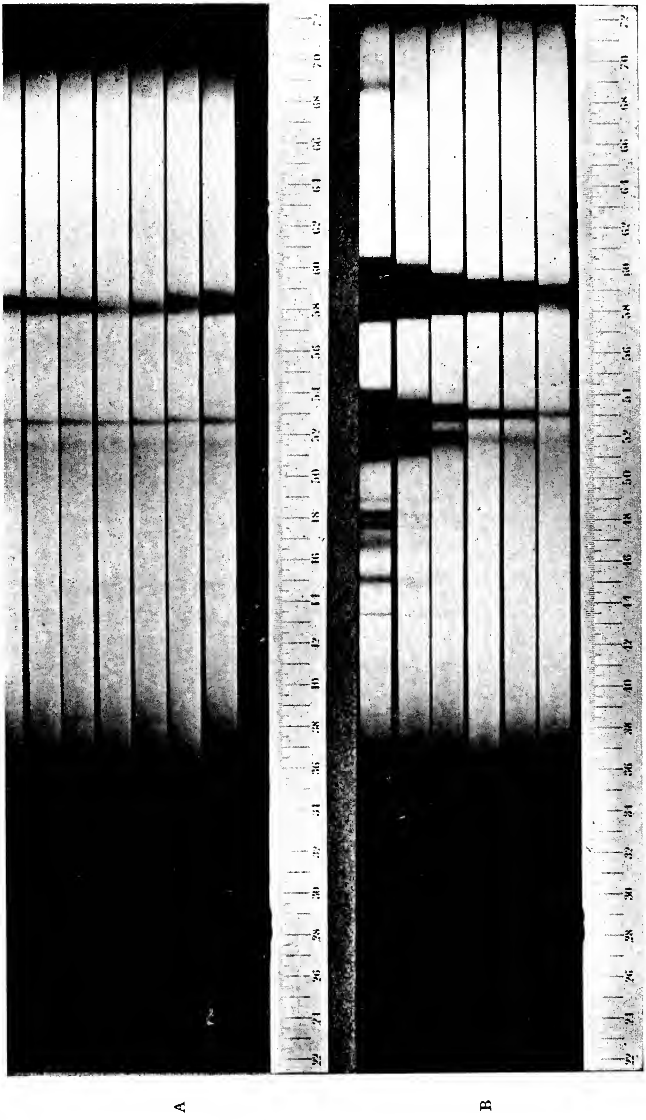
B

Plate III.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A
B

seemed of interest to photograph the absorption spectra of a salt when different amounts of an acid were added to the given salt in solution. *In the case of uranyl salts several were found to have different absorption spectra.* In the case of neodymium, however, it was found that the various salts had practically the same absorption spectra. The absorption of the acetate was, however, found to differ from that of the other salts, so that the chemical changes produced by adding various acids were photographed with the aid of the spectroscope.

Plate III, *B*, represents the absorption spectra of an aqueous solution of neodymium acetate, the concentration being kept constant and only the depth of cell being changed.

It will be seen from a mere glance that the absorption spectrum of the acetate is quite different from that of the other neodymium salts. All the bands are much wider and less intense. Many of the broad bands that appear as several finer bands in the spectra of the other salts appear here as single and very weak bands when the depth of cell is small.

The following are the wave lengths of a few of the bands: $\lambda\lambda$ 3485, 3520, 3820, 4040, 4200, 4295, 4333, 4360, 4460, 4630, 4720, 4770, 4850, 5140 (very wide and weak), 5260, 5360, 5660, 5800 to 5860, 6820, and 6950.

It will be noticed that all the bands are 10 to 20 Angström units farther to the red than the corresponding bands of the other neodymium salts.

Section *A*, of Plate III, represents the effect of adding nitric acid to a solution of neodymium acetate. The first strip of *A* represents a solution containing nitric acid and shows that the acetate bands have been shifted some 10 Angström units towards the violet by this addition of acid. This shift occurs before any other change of the acetate bands takes place.

Plate III, *A*, represents a spectrophotograph of the effect of adding nitric acid to an aqueous solution of neodymium acetate. The addition of nitric acid causes the absorption in the ultraviolet to increase. The general effect on the neodymium bands is to cause the bands to become sharper.

and, then, as more and more acid is added, to make the bands diffuse again. When the bands are sharpest they are practically the same as the bands of neodymium nitrate in water. It requires the addition of a very considerable amount of nitric acid to produce the nitrate neodymium bands.

The group of bands in the region λ 3500 in the first and seventh strips appears to be slightly displaced to the red. In fact, all the "nitrate" bands of the third and fourth strips are some 10 Angström units farther towards the violet than the bands of the first and seventh strips.

Strip 1.	Strip 3.	Strip 7.
3470	3465	3470
3510 very fuzzy	3505	3515 very fuzzy
3550	3533 sharp	3550
4285	3553	4285
4705	4275	4705
	4695	

In strip 1 there is a strong band at λ 5230 to λ 5250. In strip 2 appears a very fine and weak band on the shorter wave-length side of the white band at λ 5240. In strips 3 and 4 the two bands are of equal intensity and are located at λ 5225 and λ 5234. In strip 5 a band appears on the red side of λ 5234. At the same time λ 5234 has become very much stronger than λ 5225. In strip 7 λ 5225 has become very weak. In strip 7 there are weak and fine bands at λ 5205, and λ 5225, and a band from λ 5230 to λ 5250.

The group of bands at λ 5800 behaves in the same way. In strip 4 there are bands at λλ 5730, 5755, 5775, 5800, and 5820. In strip 1 is a hazy band at λ 5750 and others at λλ 5790, 5820, and 5870. In strip 7 there are four bands, two at λ 5730 to 5760 and two at λ 5770 to 5830. The bands λλ 6800, 7040, and 7100 appear only in the central strips.

A spectrogram was made to show the coexistence of the "water" and "alcohol" bands of neodymium chloride. It is shown in Plate V, *A*. Anhydrous neodymium chloride was dissolved in a mixture containing 8 per cent. water and 92 per cent. ethyl alcohol. The first four strips represent a Beer's law run, the concentrations being 0.5, 0.3, 0.1 and 0.05 normal, the most concentrated solution being the one

Plate IV.


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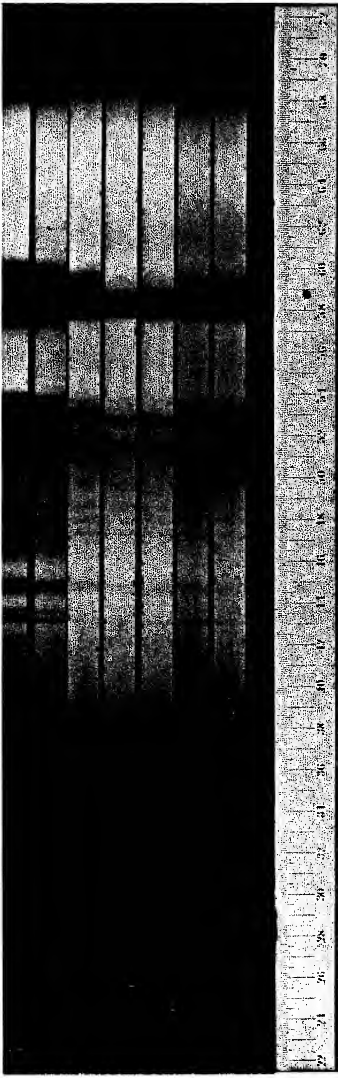
Plate V.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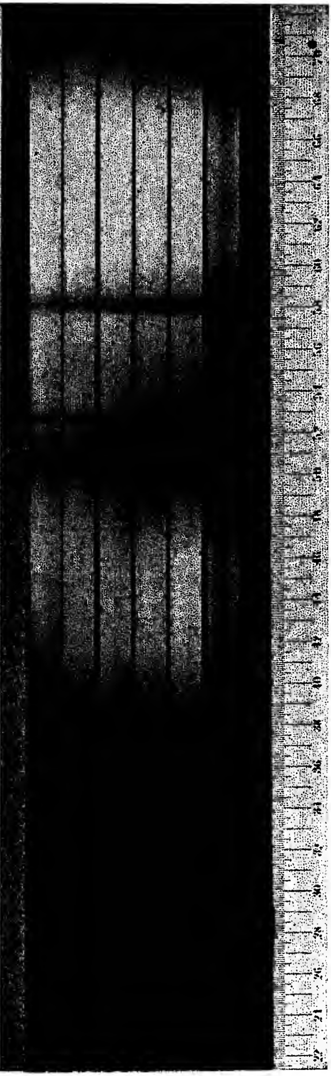
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whose spectrum is next to the scale. The last three strips represent a constant concentration where the depth of cell is increased.

The spectrogram shows that Beer's law does not hold, the more concentrated solutions being the greater absorbers. This is especially true of the alcoholic portion of the absorption. In strip 1 the "alcoholic" band corresponding to the "water" band λ 4274 has about the same intensity as the "water" band. In strip 4, however, the "alcohol" band has become very weak, indeed, while the "water" band has slightly increased in absolute intensity as compared with strip 1. Several other bands indicate the same change. The "alcohol" bands thus weaken in intensity as the concentration is decreased, while the "water" bands do not.

In this connection experiments are now in progress in which it will be tested whether changes in temperature, the addition of chemical reagents, etc., affect the different bands in the same way.

Plate V, *B*, represents the effect of adding hydrobromic acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of a solution of neodymium acetate in water to which about a drop of hydrobromic acid has been added. Strip 2 represents the same to which several more drops of hydrobromic acid have been added. The remaining strips represent the absorption of the same solution to which more and more hydrobromic has been added.

The first strip gives the characteristic acetate spectrum. In order to show the effect of the acid the wave lengths of the bands of the acetate measured on the film itself are given and compared with the spectrum of strip 2.

Strip 1.	Strip 2.
....	3465
....	3510
....	3543
....	3560
4290	4285
4450	4445 4460
4715	4705
4775	4775
4800 to 5150 gen. absorp.	4830 5105 5140
5240	5225 5240
5745	5740
5760	5760
....	5775
5790	....
5825	5810
5870	....

The effect of adding a very small amount of hydrobromic acid is very pronounced. The addition of larger amounts of hydrobromic acid has very little effect. The shifting effect of hydrobromic acid is very small as compared with the same effect produced by nitric acid on the nitrate. The presence of a large amount of hydrobromic acid does not make the bands hazy and wide.

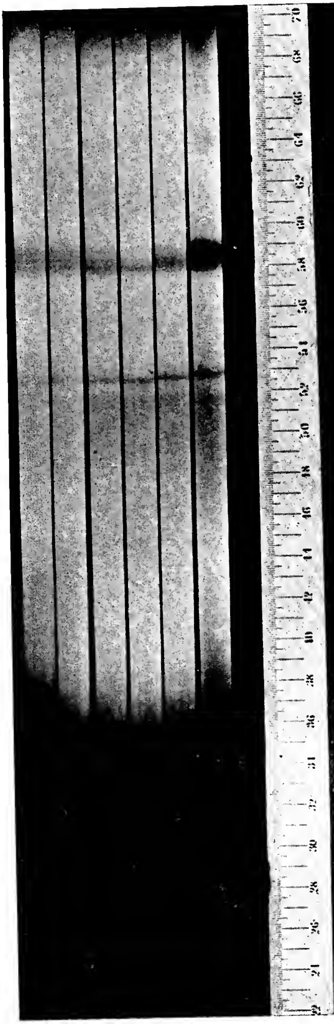
Plate VI, *A*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of the pure aqueous solution of the acetate. The second strip represents the absorption of the same to which one drop of hydrochloric acid has been added. The third strip represents the absorption of the solution to which two more drops of acid have been added The acid used was concentrated. The following table represents in part the changes which the addition of acid has caused to take place.

It will be seen that the addition of but a small amount of acid caused the appearance of a large number of fine bands, especially in the region of λ 5800. It also caused a very considerable shift of all the bands to the violet, an action similar to that of nitric acid. Further addition of acid brought out a spectrum very similar to that of neodymium chloride as shown by strips 3 and 4. Still further addition of acid produces other changes, one being the appearance of new bands in the region λ 5900.

Plate VII, *A*, gives a spectrogram where known amounts of hydrochloric acid were added to an aqueous solution of neodymium acetate.

Strip 1.	Strip 2.	Strip 3.	Strip 6.
3485	3465	3465(s)	The whole group is very weak and diffuse
3530	3510	3510	
3560	3540	3540 s	
....	3560	3560	
....	....	3580	
4297	4285	4285	4285 very weak 5303 very weak 5350 very weak

Plate VI.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Table—(Continued).

Strip 1.	Strip 2.	Strip 3.	Strip 6.
	4710 4775 4845	4710 4775 4845	
5140	5110 5140	....	
5260	5225 5245 5235	5230 s 5245 s	5230 very weak 5245 very weak
5760	5740	5740	5750
5810	5760	5760	5785
5850	5780	5780	....
	5795	5810	5815
	5815		5900
	5830		5930
	5865		
	5870		
	5895		
	5910		

A spectrogram (Plate VI, *B*) was made of mixtures in various proportions of neodymium acetate and neodymium chloride in water. Strip 1 is for the pure acetate and strip 7 for the pure chloride. The intermediate strip represents mixtures, the amount of chloride increasing from the bottom upwards. The concentration of neodymium was kept constant.

From this spectrogram evidence is obtained that each of the two salts has its own spectrum. As the amount of acetate is decreased the acetate bands gradually decrease in intensity and finally disappear. At the same time the chloride bands increase in intensity.

The band λ 5225 apparently is a chloride band, and does not appear in the acetate solution. On the other hand, the band λ 5830 and the very diffuse band λ 5860 appear to be acetate bands, and gradually disappear as the amount of acetate decreases.

A question which was raised by a study of some of the other spectrograms was whether by the addition of hydrochloric acid to the acetate different chemical compounds were formed. In the above spectrogram only two sets of bands appear, and it thus seems very probable that when hydrochloric acid is added to the acetate more than two compounds exist, for there are more than two sets of bands. Indeed, it seems probable that there *is a whole series of compounds or systems formed between the acetate on the one hand and the chloride on the other.*

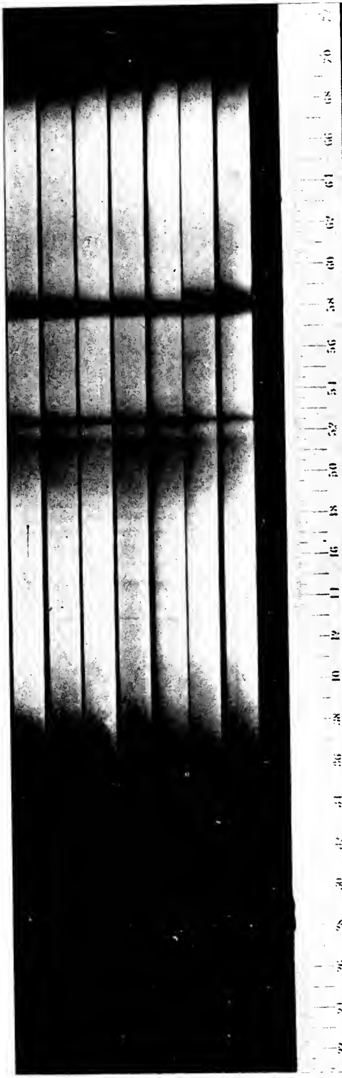
Plate VII, *B*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium citrate. The absorption spectrum of the citrate is very similar to that of the acetate, and the changes in the absorption spectra are very similar to those that take place when mixtures of the acetate and chloride are dissolved in water. In other words, there are bands here—"citrate" bands—which are very similar to the "acetate" bands. As hydrochloric acid is added the characteristic "citrate" bands gradually decrease in intensity while the "chloride" bands increase in intensity. There is no evidence here of more than two chemical compounds.

Summary.

No salts show the complexity of absorption spectra better than those of neodymium and erbium. Some of the bands are wide and diffuse, some narrow and strong—in fact, bands of very great diversity of appearance are present. In any given solvent the absorption spectra of the various salts are very similar and in many cases practically identical. But when the solutions are very concentrated or when the salts themselves are investigated, it is found that the absorption spectra are entirely different for each salt. The fact that the absorption of different salts in the same solvent is very similar is a strong argument *that the solvent plays a very important rôle in the absorption of light.* This view is very much strengthened when it is found that the absorption in different solvents is different, and that in mixtures of solvents both solvent bands coexist.

During the work on the absorption of uranyl nitrate to which sulphuric acid was added, the very fine banded absorption spectra of nitric oxide were obtained. From the conditions of the experiment it seems very probable that this nitric

Plate VII.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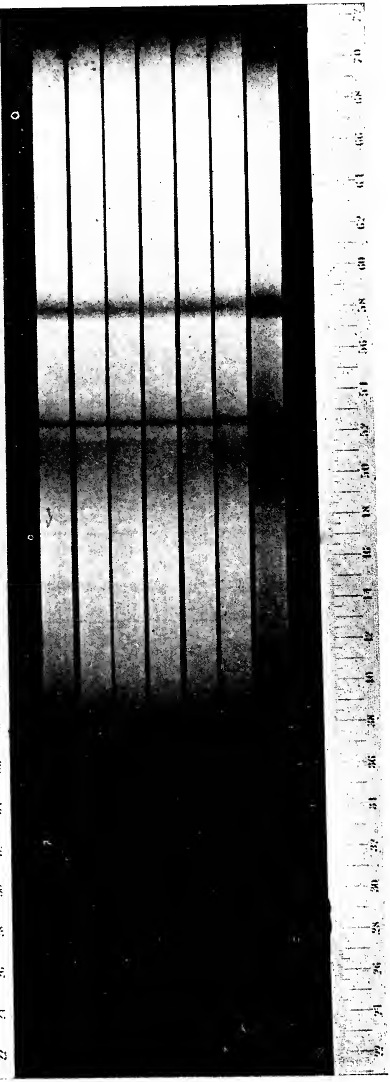
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oxide was in solution. Granting that this is the case, the experiment shows that the solvent itself under some conditions may not have any effect upon the absorption spectra. It seems reasonable to suppose that it is when chemical combination between solvent and solute takes place that the absorption of light is greatly modified.

In the case of neodymium bands it is very difficult to change the wave length of the bands. Becquerel and others show that there are small changes as the neodymium is cooled to very low temperatures. The absorption spectra of salts at 600° show but slight changes in wave length compared with the salts at 0°. For some bands the shift is about 10 Angsröm units. Our work shows practically no shift in the absorption bands of pure aqueous solutions between 0° and 90° C. However, when calcium or aluminium is present, in some cases there are shifts.

The absorption spectrum of neodymium chloride has been photographed in glycerol and alcohol solutions. There are indications of "alcohol" and "glycerol" bands. The latter are more persistent than the alcohol bands. In the case of glycerol there seemed to be one band that gradually shifted from the water to the glycerol position, indicating the possibility of the existence of intermediate glycerolates.

The effect of free nitric acid on the bands of neodymium nitrate is to cause them to become much broader and more diffuse than the bands of the neutral salt. Some of the bands are caused to broaden more on the red than on the violet side. The effect of free nitric acid on the neodymium bands is thus very different from the effect on the uranyl nitrate bands.

Early in the work it was intended to alter conditions so that each band could be followed throughout the various changes that it underwent. In most cases, however, this is at present very difficult to do, on account of the very sudden changes in the character of the spectra, and in many cases also on account of the diffuseness of the bands. For instance, the band λ 4274 is certainly one of the most characteristic bands of the water spectrum. In glycerol it is found that apparently this band gradually shifts to λ 4288 for a pure glycerol solution. For solutions containing a large amount there appear fine satellites at λ 4270 and λ 4305. In alcohol the band appears at λ 4290. The band λ 4274 does not, however, shift into the alcohol band. In a solution of neodymium nitrate in water as made by Anderson there appear two strong bands close together, the distance between the opposite edges being about 10 Angström units, and between the adjacent edges, 2 Angström units. Neodymium nitrate and sulphate crystals each give two strong components, but in this case the distance between the opposite edges is 15 Angström units, and between the adjacent edges 6 Angström units. In other words, in the neodymium nitrate crystal the components are farther apart than in the nitrate solution as made by Anderson. In the solutions made by Jones only one component appears. A remarkable result manifests itself when the water of crystallization of the sulphate and nitrate crystals is driven off. The rather paradoxical effect is to cause the "λ 4274" bands to become weaker and appear as a single band. In the case of neodymium nitrate, driving off the water of crystallization causes many of the bands to be shifted towards the red. For the sulphate this drying results in a shift of some bands to the violet, while other bands remain unshifted. The dry nitrate bands in several photographs made by Anderson are all of some 50 Angström units greater wave length than the dry chloride, dry sulphate, or crystalline sulphate bands. It is at present premature to attempt to interpret these changes, since the intermediate steps have not been followed. Much work remains to be done in this direction.

In aqueous solutions it has been found that the absorption of neodymium acetate is different from that of the chloride, bromide and nitrate. Photographs have been obtained of the spectrum as the acetate was changed to another salt by the addition of inorganic acids. These spectra indicate that *in some of the reactions there probably exist several systems or compounds between the acetate and the salt of the acid added.*

Description of Plates I to VII.

Plate I. *A.* Neodymium Chloride in Glycerol. Cell depth constant, 9 mm.
Concentrations, 0.84, 0.63, 0.42, 0.28, 0.196 and 0.105 normal.

B. Neodymium Chloride in Glycerol. Cell depth constant, 3 mm.
Concentrations, 0.105, 0.143, 0.196, 0.28, 0.42 0.63 and 0.84 normal.

Plate II. *A.* Neodymium Chloride in Glycerol and Water. Cell depth, 2.2 mm.
Concentrations, 0.84, 0.80, 0.76, 0.67, 0.59 normal.
Percentages of water, 0.5, 10, 20, 30, 60, 90.

B. Neodymium Chloride in Glycerol and Water. Cell depth, 32.5 mm.
Concentrations, 0.59, 0.67, 0.76, 0.80, 0.84 normal.
Percentages of water, 90, 60, 30, 20, 10, 5 and 0.

Plate III. *A.* Neodymium Acetate to which Nitric Acid is Added. Cell depth, 30 mm.
Concentration of Neodymium Acetate, 0.041 normal.
Concentration of Nitric Acid, 0.117, 0.234, 0.585, 1.17, 4.09, 8.18 and 16.36 normal.

B. Neodymium Acetate in Water. Concentration, 0.041 normal.
Depth of cell, 1, 2, 3, 6, 14 and 34 mm.

Plate IV. *A.* Neodymium Chloride in Glycerol, 0.15 normal.
Temperatures, 20°, 60°, 110°, 150° and 180° C.

B. Neodymium Nitrate in Concentrated Nitric Acid. Concentration, 0.4 normal.
Depth of cell, 0.2, 0.8, 2, 6, 16 and 32 mm.

Plate V. *A.* Neodymium Chloride in Water and Ethyl Alcohol.
Solution contained 8 per cent. of water.
Strips 1, 2, 3, 4, Beer's law. Concentrations of neodymium chloride, 0.5, 0.3, 0.1 and 0.05 normal. Strips 5, 6, 7, concentration 0.5 normal.

B. Neodymium Acetate in Water. Strip 1 represents the neodymium acetate in water. Succeeding strips show the effect of adding more and more hydrobromic acid.

Plate VI. *A*. Neodymium Acetate in Water, 0.041 normal.
Strip 1, pure aqueous solution. Strip 2, the same, to which one drop of hydrochloric acid has been added. Succeeding strips represent the addition of more and more hydrochloric acid.

B. Mixture of Neodymium Acetate and Neodymium Chloride in Water. Strip 1, all neodymium acetate. Strip 7, all neodymium chloride.

Plate VII. *A*. Neodymium Acetate in Water. Cell depth, 30 mm.
Concentration of acetate, 0.041 normal. Concentration of hydrochloric acid, 0.113, 0.226, 0.566, 1.13, 3.95, 7.91 and 15.82 normal.

B. Neodymium Citrate in Water. Cell depth, 30 mm.
Strip 2 and succeeding strips show the effect of the addition of hydrochloric acid.

(*The second part of this article will appear in the February number of* THIS JOURNAL.)

SELECTIVE OXIDATION.

BY HARRY C. JONES AND W. W. STRONG.

[THIRTY-THIRD COMMUNICATION.]

This is part of an investigation being carried out with the aid of a grant from the Carnegie Institution of Washington.

The power of solutions to absorb light enables us to distinguish between the parts of the dissolved salt combined with each solvent in a mixture of two solvents. If uranous bromide, obtained by the reduction of uranyl bromide with nascent hydrogen, is dissolved in a mixture of methyl alcohol and water we have two well-defined sets of absorption bands. One set is characteristic of the uranous salt dissolved in water and is what we term uranous "water bands." The other set is characteristic of the uranous salt dissolved in methyl alcohol, and we term these the uranous "methyl alcohol bands."

If we add certain oxidizing agents which are soluble in both water and methyl alcohol, the portion of the salt combined with water is oxidized and the part combined with alcohol remains unchanged. This is shown by the fact that the "water bands" entirely disappear and the "alcohol bands" remain practically unchanged.

The experiment as actually carried out was the following: To two parts, by volume, of a solution of uranous bromide in water was added one part of water and six parts of methyl alcohol. The absorption spectra of this solution showed the bands of the "hydrated" uranous bromide and the bands of the "alcoholated" uranous bromide. A small amount of sodium perchlorate dissolved in methyl alcohol was added to the above solution. Sodium perchlorate is, of course, soluble in both methyl alcohol and water. There was usually a small amount of hydrobromic acid present from the reduction of the uranyl to the uranous salt. This would, of course, liberate perchloric acid which would be the real oxidizing agent. The result is that the uranous "water bands" disappear, showing that the uranous salt, bromide or perchlorate, had been oxidized to the uranyl condition. The "water bands" that disappear have the following wave lengths:

λ 4850, λ 4970, λ 5500, λ 6420, λ 6750.

The uranous "methyl alcohol" bands do not disappear, their intensities being practically the same as before the addition of sodium perchlorate. The more prominent of these bands have the following wave lengths:

λ 4900, λ 5020, λ 5260, λ 6220.

An experiment was carried out which was similar to the above, but in which a different oxidizing agent was used. Uranous bromide was dissolved in a mixture of methyl alcohol and water and calcium nitrate dissolved in methyl alcohol was added to the solution, calcium nitrate being soluble in both of the above solvents.

In this case the "water" bands disappeared entirely, and the intensity of the "alcohol" bands was not diminished in the least. These oxidizing agents, although soluble in both of the solvents present, are capable of oxidizing the part of the uranous salt that is combined with water—the hydrated salt—but are incapable of oxidizing the part of the salt that is combined with alcohol—the alcoholated uranous salt. When hydrogen dioxide is used as the oxidizing agent, both the "hydrated" uranous bromide and the "alcoholated" uranous bromide are oxidized to the uranyl condition. Selective oxidation is shown by calcium nitrate and by sodium perchlorate, but not by hydrogen dioxide.

Similar results were obtained with uranous chloride. When calcium nitrate is added to a solution of uranous chloride in a mixture of water and methyl alcohol the "hydrated" uranous salt is oxidized and the "alcoholated" salt remains practically unchanged. When potassium chlorate is added to a solution of uranous chloride in a mixture of water and methyl alcohol, the absorption bands corresponding to the "hydrated" salt weaken very greatly in intensity, while the bands corresponding to the "alcoholated" salt do not show the slightest diminution in intensity. Potassium chlorate is only slightly soluble in methyl alcohol. Both the "hydrated" and "alcoholated" salt are completely oxidized by hydrogen dioxide.

The comparatively slow transformation of the "alcoholated" uranous salt into the "hydrated" salt is probably due to the presence of the uranyl ions in the water.

Physical Chemical Laboratory,
Johns Hopkins Univ., Nov., 1910.

THE ESTERIFICATION OF BENZAMIDE AND THE PREPARATION OF *N*-SUBSTITUTED BENZAMIDES.

By E. Emmet Reid.

Over fifty years ago, Kundig,[1] working in Kekulé's laboratory, noticed the production of ethylamine in a mixture containing alcohol and acetamide. Thirty years later, Bonz,[2] at the suggestion of Lothar Meyer, undertook a thorough study, quantitative as well as qualitative, of the reversible reaction

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[1] Ann. Chem. (Liebig), **105**, 277 (1858).

[2] Z. physik. Chem., **2**, 865–900 (1888).

$$(1)\quad CH_3CO\vdots\underline{NH_2 + H}\vdots OC_2H_5 \rightleftarrows CH_3COOC_2H_5 + NH_3.$$

In the reaction product he identified ethylamine, obtaining 0.343 gram of it from 10 grams of acetamide, and concluded that ethylacetamide was also present though he did not isolate it. He assumed that the amine was produced by the action of ammonia on the ester previously formed, thus:

$$(2)\qquad CH_3COOR + NH_3 = CH_3COONH_3R$$

He offered no evidence for this view but did show that the amine was produced immediately when alcohol was heated with pure acetamide. His results are more simply accounted for by supposing that the amide and alcohol react directly to form a *N*-substituted acetamide:

$$(3)\quad CH_3CONH\vdots\underline{H + HO}\vdots C_2H_5 = CH_3CONHC_2H_5 + H_2O.$$

He encountered great difficulties in estimating the amounts of amine and of substituted amide formed and practically gave up this part of the problem. A number of alcohols and aliphatic amides gave exactly similar results.

Romburgh,[1] Wheeler,[2] and many others have made substituted amides by the action of an acid chloride on the proper substituted amine.

Titherley[3] prepared a number of *N*-substituted amides by treating sodium amides with potassium alkyl sulphate.

In connection with a study of certain other equilibria,[4] I tried the action of alcohol on benzamide and, while the primary object was not attained any more than in the work of Bonz, yet ethylbenzamide was obtained so readily and in such quantity as to suggest this as a convenient method of preparing some, at least, of the alkylbenzamides. Further work has confirmed this supposition. The amines obtained as by-products are valuable and may be made the main object in the preparation.

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[1] Rec. trav. chim., **4**, 388.

[2] This Journal, **21**, 190; **23**, 139, 142.

[3] J. Chem. Soc., **79**, 406.

[4] This Journal, **43**, 489; **44**, 76.

EXPERIMENTAL.

Benzamide (0.2739 gram) and 0.1840 gram of 100 per cent. alcohol, sealed up in a hard-glass tube, were heated 65 hours at 200° to 210°. The reaction product was a clear, homogeneous, thick liquid which did not solidify at —20°. The contents of the tube were poured into water and titrated with 0.1 N acid of which 1.18 cc. was required. Ethyl benzoate and ethylamine were recognized. The mixture was distilled with magnesium hydroxide into some of the same standard acid, and volatile base was obtained which neutralized 6.90 cc. After titration this was redistilled into pure hydrochloric acid and this evaporated to dryness by which process a crystalline residue was obtained which dissolved quickly and completely in 2 cc. of absolute alcohol and showed other properties of ethylamine hydrochloride. The ether extract of the alkaline residue from the first distillation yielded an oil which crystallized on rubbing and then melted at 65°.5–66°.2. The melting point of ethylbenzamide is variously given as 68°–69° and 71°. A single ether extraction of this same liquid, after acidifying, yielded enough benzoic acid to neutralize 5.00 cc. of 0.1 N alkali. Since the benzamide used was equivalent to 22.63 cc. of the standard acid, 1.18/22.63 or 5.27 per cent. of the amide had reacted with the alcohol according to equation (4):

$$(4)\quad C_6H_5CO\underline{\vdots NH_2 + H\vdots}OC_2H_5 \rightleftarrows C_6H_5COOC_2H_5 + NH_3.$$

Since no benzamide was found, but in its place practically pure ethylbenzamide, reaction (5) must account for the other 94.73 per cent.:

$$(5)\quad C_6H_5CONH\underline{\vdots H \qquad HO\vdots}C_2H_5 = C_6H_5CONHC_2H_5 + H_2O.$$

Supposing this to have gone to completion there would have been present in the tube 2.263 — 0.118 = 2.145 millimoles of ethylbenzamide and an equivalent amount of water. These would then react according to the reversible reaction (6), finally reaching equilibrium:

$$(6)\quad C_6H_5CONHC_2H_5 + H_2O \rightleftarrows C_6H_5COONH_3C_2H_5.$$

Equilibrium was reached when 26.7 per cent. of the amide has been transformed into the ethylammonium salt. For benzamide and water the limit was found at 25.2 per cent.[1] though the close agreement is accidental, since the limit very likely varies with the temperature as Menschutkin[2] found for aliphatic amides. The data for this sample and for five others which were heated at the same time with it but which were not analyzed for seven months after are given below in Table I. Some shifting of the equilibrium may have taken place in the interval. Though heated in the same tube, some of the samples were nearer the source of heat and were at a higher temperature than others, so it was to be expected that the limits would vary.

Table I. Benzamide and Ethyl Alcohol.

Benzamide, gram	0.2739	0.2836	0.3357	0.3189	0.3548	0.3063
Alcohol, "	0.1840	0.2153	0.1839	0.1704	0.1610	0.1572
Amide, millimoles	2.262	2.342	2.772	2.633	2.930	2.529
Alcohol millimoles	3.996	4.675	3.974	3.700	3.496	3.414
Ester, per cent	5.27	1.55	0.36	0.53	0.17	0.91
Hydrolysis, "	26.7	35.2	21.5	24.7	19.6	......

In the first sample the titration of the reaction mixture was made with cochineal, which accounts for the high value obtained for the ester, since this indicator is not sufficiently sensitive to benzoic acid, changing color only for a considerable concentration of that acid. The titrations in the other cases were made with phenolphthalein. It will be noted that the amount of ester varies roughly with the excess of alcohol used in making the mixture. This is what would be expected, since whatever the course of the reaction at first, ultimately there will be equilibrium between the residual alcohol and the substituted benzamide on the one side and the ester and substituted amine on the other.

The reaction was next studied on a larger scale with a view to adapting it for use in the preparation of alkylbenzamides in quantity, but since the object was to determine the ultimate condition of things rather than to get the compounds easily and quickly, excessively long time periods were employed.

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[1] This Journal, **44,** 76.

[2] J. prakt. Chem., [2] **29,** 422–436, 445.

Since benzamide is very soluble in hot water while the alkylbenzamides are very sparingly soluble even in boiling water, benzamide can be readily extracted from the reaction product of an incomplete reaction and there is no practical need of pushing the reaction to the limit.

Since, in general, the equilibrium between an amide and water on the one side and the corresponding ammonium salt on the other shifts with change of temperature so that there is a higher percentage of amide at the higher temperature, it would be advantageous to use as high a temperature as practicable. In the present work, in which soft glass tubes were employed, the temperature was kept down on account of the rapid action of water on the glass at higher temperatures. Since there is no acid in the mixture there is no reason why an autoclave might not be used.

The benzamide was sealed up with a slight excess of alcohol in a large soft-glass tube and heated at 220°–230° for from two to seven days in the steel tube mentioned in a previous paper.[1] On opening the glass tubes, practically no pressure was ever found. The contents of a tube were poured into water and distilled with steam as long as appreciable amounts of ester passed over. The distillate was extracted twice with ether, the ethereal extract dried with calcium chloride, and evaporated at 100°, and the residue weighed as ester. The residue in the distilling flask was extracted twice with ether, the ether extract being washed with dilute acid, dilute sodium carbonate solution, and twice with water. The ether was evaporated at 100° or a little above and the residue weighed as alkylbenzamide. The aqueous portion was made alkaline and distilled into hydrochloric acid which was then evaporated to dryness and the residue after further drying at 120° was weighed. This was extracted with absolute alcohol and the residue dried and weighed as ammonium chloride. The difference of these two weights was considered the weight of the alkylamine hydrochloride present. The distillation residue was acidified, cooled to 0° and the benzoic acid filtered off, washed, dried

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[1] This Journal, **43**, 489.

and weighed. The volume of the solution and washings was measured and the amount of benzoic acid remaining in solution calculated from its solubility (1.5 grams per 100 cc.) as given by Ost.[1]

The *N*-substituted benzamides remaining when their ether solutions were evaporated appeared as thick, colorless or slightly colored oils which solidified to solid masses of crystals. In the cases of the ethyl and propyl compounds, the solidification was rapid when once started and evolved considerable heat. Most of the data obtained are given below in Table II, but preceding that is a description of each experiment.

Experiment 1. Methyl Alcohol and Benzamide.—The mixture was heated for 69 hours at about 220°. When cool, the tube contained a thick, apparently homogeneous, slightly yellow liquid with a mere trace of thin rectangular plates suspended in it. After remaining liquid for nearly seven months, the contents of the tube solidified almost completely into a mass of thick transparent needles several inches in length. On pouring the mixture into water an acid, not an alkaline, mixture was obtained. All of the other experiments gave alkaline mixtures. In this case no attempt was made to obtain any ester. The methylbenzamide left on evaporation of the ether was pasty while all the others were solid. On pressing on paper, it gave a good melting point which was raised to 79°.8 by one crystallization from boiling water. Wheeler gives 80°–81° as its melting point.

Experiment 2. Ethyl Alcohol and Benzamide.—In this experiment the time was 68 hours and the temperature about 215°. The ester and amine were distilled off with magnesium hydroxide and steam, and the ethylbenzamide extracted from the distillation residue. The crude amide melted at 64°–66°.

Experiment 3. Ethyl Alcohol and Benzamide.—The alcohol used in this and in experiment 2 was of high purity and contained not more than 0.02–0.03 per cent. of water. The mixture in this case was heated 56 hours but on cooling, a considerable amount of transparent rectangular plates sepa-

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[1] J. prakt. Chem., [2] **17**, 232.

rated. It was reheated for 70 hours at about 228°. The contents then appeared as a thick homogeneous liquid which solidified nearly completely to a mass of long, transparent, colorless needles. The 0.533 gram of ester obtained was distilled and began to go over at 210°, but the boiling point rose rapidly during the distillation, showing that the substance was not pure. The melting point of the crude amide was 58° and rose to 68°–68.°5 when the product was boiled with water and allowed to solidify. The amide is slightly soluble in boiling water. Such a solution filtered boiling hot deposited the amide as clear oily drops which on standing crystallized into a rosette of beautiful pure white needles, each one a hollow tube of square cross-section with square-cut ends. These were 10–12 mm. long and several mm. thick. From 360 cc. of the solution were deposited 3.68 grams o the amide melting at 68°.8. The hot saturated solution may, on cooling, become an emulsion from which the amide is slowly deposited in beautiful fine needles melting at 69°. The melting point is variously given in the literature at from 68° to 71°.

Experiment 4. Propyl Alcohol and Benzamide.—This mixture was heated for 72 hours at about 220°, but as on cooling, it contained crystals it was reheated for 70 hours longer at about the same temperature, though for a while it was as high as 250°. On cooling, it still contained crystals which were most likely propylbenzamide since no evidence of the presence of benzamide was found on working up the product. The 2.11 grams of ester isolated was distilled and about three fourths of it went over between 229° and 233°. The boiling point of propyl benzoate is 230°.7 and the substance was practically the pure ester. To get this ester, over 600 grams of water was distilled. The crude amide seemed to contain a slight amount of oil and without even pressing on paper melted at 62°. One treatment with boiling water raised the melting point to 76°. It is soluble in about 270 parts of boiling water. Such a solution when filtered and cooled gives a white emulsion. On standing several days the amide is usually transformed into beautiful, colorless, transparent, thin, square plates (melting at 83°), leaving the mother liquor perfectly clear. Titherley by a number of crystallizations from a succession of solvents raised the melting point to 84°.5.

Experiment 5. Isobutyl Alcohol with Benzamide.—The mixture was heated at irregular temperatures up to 230° for seven days. On cooling, the contents of the tube solidified to a pure white, fibrous mass. The 3.56 grams of ester obtained appeared to be impure for though it began to boil at about the right point, the temperature rose rapidly during the distillation. To get this ester over 1260 grams of water was distilled. The crude amide, without even pressing on paper, melted at 48°–49° instead of 57°–58°, which is the melting point given in the literature. Treatment with boiling water extracted 1 gram of benzamide and raised the melting point to 50°–52°. This amide dissolves into about 1300 parts of boiling water and on cooling gives an emulsion from which the amide is slowly deposited in short, thick needles melting at 56°. By adding about ten per cent. of alcohol, the solubility is greatly increased and well-formed colorless needles up to 30 mm. in length may be obtained. Some of these melted at 56°.5.

Experiment 6. Benzyl Alcohol and Benzamide.—A mixture of 2.85 grams of benzamide and 3.10 grams of benzyl alcohol was sealed up and heated for 70 hours at about 220°. The product was a yellowish solid. Carbon dioxide escaped in moderate quantity when the tube was opened. The product was extracted with ether and the ethereal soultion shaken with acid and alkali. It yielded a considerable amount of a flaky solid, melting at 95°–100°. This was crystallized from boiling water containing a little alcohol in which it is very slightly soluble and then melted at 104°.5. Benzylbenzamide melts at 105°–106°. Considerable benzoic acid, but no benzylamine, was isolated.

The upper portion of Table II gives actual weights in grams of the substances used and isolated while just below these quantities are given in moles.

Table II.

Number of experiment Alcohol used.	1. Methyl.	2. Ethyl.	3. Ethyl.	4. Propyl.	5. Isobutyl.
Benzamide, grams	24.52	28.99	26.88	30.38	24.60
Alcohol, grams	8.058	12.02	13.25	18.74	15.29
Alkylamide, grams	10.63	21.81	19.96	29.84	24.96
Benzoic acid, grams	12.57	8.11	10.23	6.98	4.75
Amine salt, grams	5.02	2.71	5.67	4.95	0.82
Ammonium chloride, grams	0.630	...	0.694	1.514	1.41
Ester, grams	...	0.298	0.533	2.11	2.92
Benzamide, moles	0.2018	0.2394	0.2220	0.2503	0.2031
Alcohol, moles	0.2515	0.2511	0.2877	0.3120	0.2061
Alkylamide, moles	0.0797	0.1464	0.1358	0.1829	0.1410
Benzoic acid, moles	0.1030	0.0671	0.0847	0.0573	0.0391
Amine, moles	0.0744	0.0324	0.0694	0.0502	0.0075
Ammonia, moles	0.0118	...	0.0130	0.0283	0.0264
Ester, moles	...	0.0020	0.0035	0.0129	0.0163
Benzamide accounted for	0.1827	0.2155	0.2240	0.2531	0.1964
Per cent. of benzamide accounted for	90.5	90.0	100.9	101.1	96.7
Yield of alkylamide, per cent.	39.0	61.1	62.6	72.9	69.4
Yield of ester, per cent.	...	1.27	1.58	5.2	8.3
Hydrolysis of amide, per cent.	61.0	38.1	36.4	23.1	24.3

It appears from these results that the yield of alkylbenzamide is satisfactory in all cases except with methyl alcohol where the hydrolysis was too great. In this case, however, ordinary methyl alcohol containing water was used. The sum of the equivalents of the amine and the ammonia should equal the sum of the benzoic acid and the ester. In all except experiment 5 there is a shortage of bases. There is some loss of bases in distilling their benzoates in getting over the ester. In case the action of the alcohol on the benzamide were entirely complete as represented below, the ammonia found should be equivalent to the ester. The excess of the ammonia found indicates that the reactions were not quite complete. By treating the isobutylbenzamide with boiling water 1 gram of benzamide was obtained. The equivalent 0.1410 given in the table for isobutylbenzamide should therefore be 0.1352 + 0.0083 = 0.1435. This makes the equivalent of benzamide accounted for 0.1989, raising the percentage from 96.7 to 97.9.

The amount of amide transformed into the ester increases, apparently, with the molecular weight of the alcohol. The difficulty with which the alkylbenzamide is formed seems to increase with the molecular weight of the alcohol.

Since, particularly in experiments 3 and 4, the products isolated and identified account very nearly for the amount of benzamide taken we may conclude that the action of these alcohols on benzamide is represented by the two following equations, the first of which represents only a small part of the reaction in the case of the alcohols studied. However, when acid is present to neutralize the ammonia, the first equation represents the total action that takes place.

$$(1)\ C_6H_5CO\underbrace{NHH + H}_{}OC_2H_5 \rightleftarrows C_6H_5COOC_2H_5 + NH_3.$$

$$(2)\ C_6H_5CONH\underbrace{H + HO}_{}C_2H_5 \rightleftarrows C_6H_5CONHC_2H_5 + H_2O.$$

The present work shows that the final result is represented thus but the course of the reactions may not be so simple.

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[Contributions from the Chemical Laboratory of Harvard College.]

CURCUMIN.

By C. Loring Jackson and Latham Clarke.

This paper contains the final account of our work[1] on curcumin—the yellow coloring matter of turmeric. The manuscript was essentially finished early in the summer but was not sent to the press because one of our observations needed to be tested by further experimental work: in the meantime, the paper[2] on curcumin by Milobedzka, von Kostanecki and Lampe reached us, in which they give reasons for adopting the formula $C_{21}H_{20}O_6$, proposed by Ciamician and Silber,[3] in place of ours, $C_{14}H_{14}O_4$. After examining carefully the arguments for each of these formulas, we have come to the conclusion that they are right, and curcumin has the formula $C_{21}H_{20}O_6$. Our reasons for this decision are given in detail in the Experimental Part. With the abandonment of the formula with 14 atoms of carbon our conclusions in regard to the structure of curcumin are swept away and we are glad that the additional facts, which settled the formula, appeared before we had published our paper, as the waste of time from our incorrect theory is thus confined to ourselves, and does not extend to our readers.

We can confirm the statement of von Kostanecki and his associates that curcumin by gentle oxidation yields ferulic acid, as we obtained it by the action of hydric dioxide, which, we should judge, gives a neater method of preparation than the oxidation by the air in alkaline solution used by them.

Of the observations made by us, the most important for the continuation of the work was that the dimethyl ether of curcumin was obtained pure with a quantitative yield by making it in a shaking machine at ordinary temperatures instead of by heat, as done by Ciamician and Silber, whose product was principally viscous with only a very small yield of the crystalline ether. We found the melting point 137°

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[1] This Journal, **39,** 696 (1908).

[2] Ber. d. chem. Ges., **43,** 2163 (1910).

[3] Gazz. chim. ital., **27,** I, 561 (1897).

instead of 135°, as given by them. A crystalline substance was also formed in this way from hydroxylamine hydrochloride and curcumin, and it is probable, therefore, that the extremely undesirable products frequently given by curcumin are due to its great sensitiveness to heat when in presence of a solvent.

It is a familiar observation that strong hydrochloric acid turns curcumin brown; we have traced this to the formation of an addition product which was dark brown when little hydrochloric acid gas was used, but turned dull violet with an excess. It was very unstable, decomposing quickly on exposure to the air, and instantly when dropped into water, curcumin being formed. We did not succeed in getting a good analysis of it; but hydrobromic acid formed a similar compound, which was a little more stable, and from this we got a result which came as near to $C_{21}H_{20}O_6(HBr)_3$ as could be expected. Both addition compounds can be kept in corked tubes, which prevents the escape of the acid gas.

It is highly probable that the reddish purple substance formed by the action of phosphoric oxychloride on curcumin[1] is either the addition compound with hydrochloric acid in an impure condition or is a similar substance containing chlorine and phosphorus, as it was converted into curcumin by water in the same way. To be sure it was converted by standing in a desiccator into a black substance instead of curcumin, but this can be ascribed to the further action of the phosphorus compound on the curcumin which was probably the first product of the action.

When curcumin was heated with one of the halogen acids, the methyl haloid was given off at low temperatures, followed, when the heat was raised, by a strongly smelling oily liquid which we could not obtain in large enough quantities to be handled in the usual way. The separation of a few drops of volatile oil from the accompanying acid and the drying of it for an exploratory analysis was a very difficult problem to which we devoted much time, and we thought (it now seems incorrectly) that the composition of this oil would throw much light on the structure of curcumin. Among our many

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[1] Jackson and Menke: THIS JOURNAL, **6**, 80 (1884).

attempts to solve this problem, one method which we tried without success, is, we think, worth description here as it may prove of use in other cases. The plan was to dissolve our oil in thiophene or some other liquid containing sulphur, and having in this way raised it to a manageable volume, to wash and dry the mixture in the usual way after which determinations of sulphur and iodine according to Carius would give the data necessary for settling the composition of the new substance. This promising scheme failed with us because we could find no compound containing sulphur which would mix with our product.

The wiping method, by which we finally dried the oil for analysis, has been described in another paper.[1]

EXPERIMENTAL PART.

Ciamician and Silber[2] state that they succeeded in raising the melting point of curcumin to 183° by many crystallizations alternately from methyl alcohol and benzene. Accordingly, we have made a number of attempts to raise it above 178°, the temperature observed by Menke and one of us, by the use of these solvents in the way indicated, and also with glacial acetic acid, and with chloroform, which produces finer crystals than any other solvent we have tried, but in spite of all our efforts, we have never observed a melting point above 178° (uncorr.). We are of the opinion therefore that the difference between the melting point given by Ciamician and Silber and ours is due to a difference in thermometers, and to make certain of the accuracy of the one used by us it was compared with a normal one, and found to differ from it by not more than 0°.2. As the analyses of curcumin made by Ciamician and Silber agree with those of Menke and one of us, it is evident that, if our lower melting point was caused by impurities (which we cannot admit in view of the experiments described above), the amount was not great enough to effect the analyses.

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[1] THIS JOURNAL, **44**, 438.

[2] Gazz. chim. ital., **27**, I, 561 (1897).

Formula of Curcumin.

Menke and one of us[1] in 1881 proposed for curcumin the formula $C_{14}H_{14}O_4$, based on the first accurate analyses of the substance and 5 determinations of the constituents of derivatives capable of settling the molecular weight. Ciamician and Silber[2] in 1897 announced that this formula should be replaced by $C_{21}H_{20}O_6$, because two determinations by Zeisel's method of methoxyl in curcumin and one in acetcurcumin gave results in favor of this formula but incompatible with $C_{14}H_{14}O_4$. When we took up the research a few years ago, one of our first undertakings was the study of the application of the Zeisel process to curcumin, when we found that, if the bath stood at 120°, the percentages of methoxyl found (12.31 and 12.69) corresponded to that for one CH_3O group in the formula $C_{14}H_{14}O_4$, which is 12.60; but as the temperature at which the reaction took place was increased, the proportion of argentic iodide found also increased, until at 170° and higher, 16.23 and 16.78 per cents of methoxyl were found, corresponding to the percentage for two (CH_3O) groups in the formula $C_{21}H_{20}O_6$, which is 16.85. As any volatile compound containing iodine would give argentic iodide under the Zeisel conditions, we next studied the nature of the volatile products formed by the action of hydriodic acid on curcumin. For this purpose they were collected instead of being decomposed with argentic nitrate as in the Zeisel determinations, when it was found that the substance given off at 120° had the smell of pure methyl iodide and that it was this substance is shown by the following analysis of this product dried by wiping it with moist filter paper in the way explained in an earlier paper.[3]

0.2102 gram of substance gave 0.3454 gram AgI.

	Calculated for CH_3I.	Found.
I	89.43	88.84

When, however, the process was carried on at 130°, the odor of methyl iodide was distinctly modified by that of a

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[1] THIS JOURNAL, **4,** 77 (1882).

[2] Gazz. chim. ital., **27,** I, 561 (1897).

[3] THIS JOURNAL, **44,** 438.

different substance with a sharp disagreeable smell, while at 170° to 180° the amount of this new product became sufficient for its odor to mask that of the methyl iodide completely. It was evident, therefore, that the removal of the methyl ran smoothly only at 120°, and that at higher temperatures it was accompanied, or followed, by a deeper decomposition of the curcumin, which formed a second volatile product. As we supposed this was an iodide different from methyl iodide, we inferred that the Zeisel determinations could not be used in support of any formula, and that our work had destroyed the 3 real arguments in favor of $C_{21}H_{20}O_6$, and added 2 to the analytical results which agree with the formula $C_{14}H_{14}O_4$, but are incompatible with $C_{21}H_{20}O_6$. These with our later analyses of derivatives of curcumin and rosocyanin raised the number of arguments in favor of $C_{14}H_{14}O_4$ to 14, while there were none on the other side that seemed to us worthy of use except as confirmatory arguments. We felt justified, therefore, in considering the accuracy of our formula proved.[1] The paper by Milobedzka, von Kostanecki and Lampe[2], however, contained 9 determinations in harmony with $C_{21}H_{20}O_6$ and incompatible with $C_{14}H_{14}O_4$, and although the latter formula still has the advantage, if only the number of determinations is considered, the case is very different when their quality is brought into the discussion, for we can discover no flaw in those given by von Kostanecki and his associates whereas a more careful scanning of ours shows that not one is above suspicion. Thus the 4 determinations of potassium in favor of $C_{14}H_{13}O_4K$ were made on salts prepared by boiling a solution of curcumin or rosocyanin in absolute alcohol with potassic carbonate, and it is possible that enough potassic carbonate might have dissolved in each case to raise the percentage from the 9.63 required by $C_{21}H_{19}O_6K$ to the 13.76 for $C_{14}H_{13}O_4K$. We ought, of course, to have tested this point by experiment, but in this and other cases we were thrown off our guard by the fact that all the determinations made agreed with each other and the theory.

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[1] Ber. d. chem. Ges., **38,** 2712 (1905), **39,** 2269 (1906).

[2] *Ibid.*, **43,** 2163 (1910).

The molecular weight determinations were made by the boiling-point method, and subsequent work in another field developed the fact that the conditions then in use by us were so unfavorable that no confidence could be placed in the results. The *p*-brombenzyl compound did not give a perfectly sharp melting point (76°–78°), and this may have been due to the presence of impurities in spite of the chemical purification to which it had been submitted. Finally, in the Zeisel determinations part of the methoxyl may have remained undecomposed at 120°, and the strong smelling oil given off from 120° to 160° may have been, not a new iodide as we supposed, but methyl iodide mixed with a small amount of a product containing no iodine. It is certainly strange, however, that at the temperature at which pure methyl iodide was given off, the amount corresponded to two CH_3O groups in $C_{14}H_{14}O_4$, and that the carbon, hydrogen and bromine in the *p*-brombenzyl compound also agreed with a C_{14} formula.

We have tried in this way to clear away the possible mistakes we have introduced into the chemical literature, and, while we regret them exceedingly, we feel there is some excuse for having been misled by *fourteen* coincidences.

Attention may be called here to two arguments in favor of the formula $C_{21}H_{20}O_6$. The determinations of hydrogen in curcumin (mean 5.63) come out as a rule too low for the value calculated for $C_{14}H_{14}O_4$—5.69—but in harmony with that for $C_{21}H_{20}O_6$—5.43; and the same is true of many of its derivatives. Some preliminary work on the action of hydroxylamine hydrochloride on curcumin gave a compound melting at 162°, which contained carbon 66.04, hydrogen 4.22, nitrogen 3.8, agreeing with the values for $C_{21}H_{21}O_6N$, carbon 65.80, hydrogen 5.48, nitrogen 3.66. We, however, consider our work on this substance so incomplete that these results should not be accepted until they have been tested by further experiments.

Behavior of Curcumin with Halogen Acids.

It is a familiar observation that strong hydrochloric acid turns turmeric paper brown. To study this phenomenon, some strong hydrochloric acid was added to curcumin, and the brown product washed with water, when curcumin was produced again, as shown by the reappearance of the yellow color and by the melting point 178°. Since this pointed to an addition-product destroyed by water, we next passed gaseous hydrochloric acid, dried with sulphuric acid, over finely powdered curcumin, when the yellow color of the solid changed at once to a characteristic dark brown, which later passed into a dull violet. Upon exposure of this violet product to the air it lost hydrochloric acid rapidly, passing back to curcumin. This change was practically complete in half an hour, although some color lingered for several days. If, on the other hand, the substance was kept in a corked tube, from which the hydrochloric acid could not escape, it retained its color indefinitely. Our attempts to analyze this compound by treating a weighed quantity with water gave poor results, partly on account of the rapid decomposition of the substance, and partly because our products always contained some unaltered curcumin. Passing hydrochloric acid gas into an absolute alcohol or benzene solution of curcumin gave apparently the same substance, but in no more manageable condition. It dissolves in absolute alcohol with a violet color, but this is very fugitive.

In the hope of obtaining a more stable addition compound, dry hydrobromic acid was passed over curcumin. The gas was made by the action of bromine on red phosphorus and water, passed through a tube containing moist red phosphorus to remove any free bromine, and then dried by phosphoric anhydride. The curcumin was powdered as finely as possible and the flask containing it shaken from time to time to expose the whole of it to the action of the hydrobromic acid. The curcumin changed from yellow to brown almost at the instant at which it came in contact with the acid, and this brown color was gradually converted by further action to a blackish violet. After the hydrobromic acid had acted for half an hour, some of the dark violet product was exposed to the air, when it lost the hydrobromic acid mechanically absorbed by the powder, whereas that chemically combined with the curcumin was given off slowly in dry air or a desiccator, but after long standing in the air all the hydrobromic acid was evolved, leaving curcumin, identified by its yellow color and melting point, 178°; while the same change took place more rapidly *in vacuo*. It follows from this observation that the substance is an addition compound and not formed by substitution. After it had been freed from adhering hydrobromic acid by short exposure to the air, it was analyzed by dropping a weighed quantity of it into water, which decomposed it at once. The curcumin was then filtered out, and the amount of hydrobromic acid in the filtrate determined.

0.3204 gram of substance gave 0.2692 gram AgBr.

	Calculated for $C_{21}H_{20}O_6.3HBr$.	Found.
Br	39.28	35.77

No much better result was to be expected since the substance undoubtedly lost some of the combined hydrobromic acid during its exposure to the air to free it from adhering acid, and it was made from solid curcumin, the parts of which protected by the layer of addition compound might have escaped the action of the hydrobromic acid. That the substance contained 3 or more molecules of hydrobromic acid seems to us established, as the amount of bromine found could not have been higher than that calculated, and $C_{21}H_{20}O_6.2HBr$ contains 30.18 per cent. bromine.

The dark violet substance decomposed slowly in dry air, more rapidly *in vacuo*, or when heated, forming curcumin and hydrobromic acid. The same change was produced instantly by water.

When curcumin was heated in an oil bath at 180°–200° with strong commercial hydrochloric acid, or with a distilled solution of hydrobromic acid, or hydriodic acid, a volatile oil was given off in addition to the methyl haloid but in such small quantity that it was impossible to determine its nature. It had a strong disagreeable smell, was oxidized by potassic permanganate, and decomposed on exposure to the air, turning green.

The black residue left after the action of the acid seemed to be the same in all three cases; in spite of its unpromising properties it was studied by us with the following results. When at first obtained, it was a black tarry mass, and as all attempts to crystallize it failed, it was purified by a method which had given good results with rosocyanin. For this purpose it was first extracted with ether which removed a brown substance, then the black insoluble residue was dissolved in a little alcohol and precipitated with water containing one per cent. of salt. After repeating these processes several times, the powder was washed free from salt, when it contained no halogen and melted at about 200°. It was dried at 100° for analysis.

I. 0.1297 gram of substance gave 0.3383 gram CO_2 and 0.0529 gram H_2O.

II. 0.2064 gram of substance gave 0.5441 gram CO_2 and 0.1029 gram H_2O.

	Calculated for $C_{69}H_{49}O_{17}$.	Found.	
		I.	II.
C	72.06	72.13	71.89
H	4.27	4.60	5.54

The black substance was converted into a potassium salt by adding to its moderately strong alcoholic solution a slight excess of potassic hydrate also dissolved in alcohol, when the black salt was precipitated. It was washed with very little alcohol, and then with ether, and dried in the desicccator.

0.1857 gram of salt gave 0.0794 gram K_2SO_4.

	Calculated for $C_{69}H_{42}O_{17}K_7$.	Found.
K	19.34	18.21

The formula given above agrees with the analytical results better than any other we have found but it would be absurd to claim it is established as no proof can be given that the specimens analyzed were pure, and in a substance with so high a molecular weight a difference of several atoms of carbon makes a change in the percentages which hardly exceeds the limit of experimental error, so that it is not hard to find other formulas which agree with the analyses; for instance, $C_{72}H_{56}O_{18}$ gives carbon 71.52, hydrogen, 4.63, and $C_{72}H_{49}O_{18}K_7$ gives potassium 18.56. It was an amorphous black powder melting at about 200°, soluble in methyl or ethyl alcohol, or acetone, insoluble in ether, chloroform, benzene, or toluene. It dissolved in strong sulphuric acid with a violet-red color; in a solution of sodic hydrate with a greenish brown color.

Dimethyl Ether of Curcumin, $C_{21}H_{18}(CH_3)_2O_6$.—Ciamician and Silber[1] by heating curcumin, potassic hydrate, methyl iodide and methyl alcohol on the water bath in a flask with a return condenser and a mercury valve, obtained a viscous mass, from which they succeeded in isolating a very small amount of a crystalline product, melting at 135° and giving on analysis, results agreeing with those for the dimethyl ether. In the hope of getting a better yield we carried on the reaction in the cold by placing the mixture in the shaking machine for 16 hours, after which it was allowed to stand at ordinary temperatures for three days. When in this way the reaction took place below 20°, orange yellow crystals 0.5 cm. long were formed, which melted at 137°, and subsequent crystallizations from methyl alcohol showed that this melting point is constant. This modification of the process, therefore, gives a pure compound at once with essentially a quantitative yield.

The dimethyl ether crystallizes in long orange yellow needles, melts at 137° instead of 135° as given by Ciamician and Silber, and in addition to the solubilities given by them is soluble in chloroform or acetone. With a drop of phosphoric oxychloride it turns deep bluish purple.

Action of Hydroxylamine on Curcumin.—As the use of the shaker had given such a good result with the dimethyl ether, we also tried the reaction of the hydrochloride of hydroxylamine in alcoholic solution with curcumin on the shaking machine and found that under these conditions a reaction took place but it ran so slowly that 3 months' shaking was necessary to complete it. Its progress was

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[1] Gazz. chim. ital., **27**, I, 561 (1897).

traced by testing from time to time with sodic hydrate, which gave a brown color with curcumin but not with the product of this reaction. The yellow product was purified by crystallization from alcohol.

0.1736 gram of substance gave 0.4204 gram CO_2 and 0.0660 gram H_2O.

	Calculated for $C_{21}H_{21}O_6N$.	Found.
C	65.80	66.04
H	5.48	4.22
N	3.86	3.8

Our results, therefore, agree with those calculated for the monoxime but, as our work did not advance beyond the preliminary stage, they should not be accepted without further experimental tests. The substance formed thick orange-yellow needles melting at 162°, which dissolved in sodic hydrate with a yellow color, but were unaffected by an aqueous solution of sodic carbonate. If an alcoholic solution of curcumin was heated on the steam bath with hydroxylamine hydrochloride for an hour or more, a yellowish white product was formed, which from its melting point, 163°, crystalline form, and the following analysis may be identical with the preceding in spite of the difference in color.

0.2381 gram of substance gave 6.4 cc. N_2 at 20° and 766 mm.

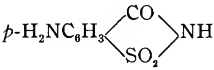
	Calculated for $C_{21}H_{21}O_6N$.	Found.
N	3.86	3.09

The isoxazole obtained by Ciamician and Silber under similar conditions is evidently different from our product as it melted at 173° and contained 69.15 per cent. of carbon.

A STUDY OF ORTHOAMINOPARASULPHOBENZOIC ACID WITH SPECIAL REFERENCE TO ITS FLUORESCENCE.

By J. H. Kastle.

Sometime ago my attention was directed to *p*-aminobenzoic sulphinide,



$p\text{-}H_2NC_6H_3\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$, as a substance suitable for the preparation of screens for revealing the presence of ultraviolet light. As is well known, aqueous solutions of this compound exhibit a bluish purple fluorescence in ordinary white light. When some of this substance, moistened with water, was placed in the path of the ultraviolet rays from an iron arc, it was observed to exhibit a beautiful bluish purple fluorescence.[1] If, however, *p*-aminobenzoic sulphinide is moistened with concentrated hydrochloric acid, instead of water, no fluorescence is observed when the mixture is brought into the path of the ultraviolet rays. In solution in concentrated hydrochloric acid this compound also shows no fluorescence in ordinary light. One would naturally imagine, I think, that the destruction of the characteristic fluorescence of this compound by means of hydrochloric acid is associated in some way with the formation of a hydrochloride, the ions of which are no longer fluorescent. The fact that the substance contains an amino group serves, of course, to strengthen such a supposition. On the other hand no hydrochloride of *p*-aminobenzoic sulphinide has ever been isolated and thus far I have been unable to obtain such a compound. The matter is further complicated by the fact that the aminobenzoic sulphinide contains an imino group which might, of course, be altered in such a way by the hydrochloric acid as to involve a change in the physical and chemical properties of the compound, among them its power to fluoresce. There are, therefore, considerable difficulties involved in the way of determining precisely why solutions of this compound lose their power to fluoresce in the presence of hydrochloric acid. About the time that these difficulties came to be recognized, I happened, in the

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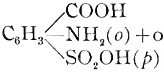
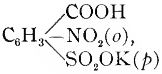
[1] *The After-glow of Benzoic Sulphinide in Ultraviolet Light.*—The striking fluorescence of *p*-aminobenzoic sulphinide in ultraviolet light naturally led me to test the conduct, in the path of these rays, of such other sulphinides as I happened to have on hand. So far as I was able to observe *p*-nitrobenzoic sulphinide showed no fluorescence and neither did the parent substance, benzoic sulphinide, but after exposure to ultraviolet light the latter compound became luminescent and continued to shine with a pale whitish light for some time after the source of the ultraviolet light had been cut off. In this connection may be mentioned the fact that crystals of benzoic sulphinide emit light when crushed. So far as I am aware, however, its peculiar conduct in ultraviolet light has never been observed prior to this time, and I hope when the opportunity presents itself to make a more thorough investigation of this phenomenon and also of the conduct of other sulphinides in ultraviolet light.

course of my reading, to note that, according to Hart,[1] *o*-amino-*p*-sulphobenzoic acid and its barium salt exhibit a strong blue fluorescence in their aqueous solutions. It, therefore, occurred to me that by reason of its simpler constitution, this compound would perhaps afford a better starting point in the attempt to determine the influence of simple chemical changes on fluorescence.





o-*Amino*-p-*sulphobenzoic Acid*, $C_6H_3\left\langle\begin{matrix}COOH\\NH_2(o)\\SO_2OH(p)\end{matrix}\right. + 0.5H_2O$.—In the preparation of this acid, Hart's general directions were carefully followed with the exception that in the oxidation of the potassium salt of *o*-nitrotoluenesulphonic acid by alkaline permanganate the required amount of the potassium permanganate was added all at once, instead of in small quantities at a time as recommended by Hart. In other words, in the oxidation of potassium *o*-nitrotoluenesulphonate I found it convenient to follow a method which I had previously employed in the oxidation of potassium *p*-nitrotoluenesulphonate. According to this, 10 parts by weight of the potassium salt of *o*-nitrotoluenesulphonic acid, and 3 parts by weight of solid potassium hydroxide are dissolved in 500 cc. of water and to this solution 22 parts, by weight, of finely powdered permanganate are added. The mixture is then heated on a water bath for 8 to 10 hours with occasional shaking. At the end of this time a small quantity of alcohol is added to destroy the excess of permanganate and the mixture filtered to remove the hydrated oxide of manganese. The clear, golden yellow filtrate is then evaporated to small bulk and strongly acidified with concentrated hydrochloric acid. In this way a good yield of the acid potassium salt of *o*-nitro-*p*-sulphobenzoic acid, $C_6H_3\left\langle\begin{matrix}COOH\\NO_2(o),\\SO_2OK(p)\end{matrix}\right.$ is obtained. This is then dissolved in strong ammonia and reduced with hydrogen sulphide, in the manner described by Hart, and evaporated to dryness. The residue is then extracted with

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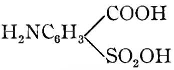
[1] This Journal, **1**, 354 (1880).

small amounts of warm water and filtered in order to remove the sulphur. The filtrate is then acidified strongly with hydrochloric acid, when the amino acid separates in crystalline condition. As described by Hart, it crystallizes in beautiful rhombic plates of a yellowish color. This yellowish color has been found to be due to impurities, since after several recrystallizations of the acid from water, containing small amounts of animal charcoal, I have obtained it in perfectly colorless condition. One would also be inclined to believe from Hart's description that the acid is anhydrous, whereas, as a matter of fact, it contains one half of a molecule of water of crystallization. That such is the case was first brought to my notice by reason of the fact that 0.217 gram of the air-dried acid required only *19.15* cc. 0.1 N sodium hydroxide for neutralization, whereas, if it were anhydrous, this quantity of the acid should actually require *20* cc. On the other hand, if the acid contains half a molecule of water it has a molecular weight of 226 instead of 217, and, hence, 0.217 gram of the air-dried acid would require only 19.19 cc. 0.1 N caustic soda. In order to determine, therefore, whether the acid is hydrated 0.1511 gram was heated in the air bath at 160° for 1 hour. It lost 0.0063 gram, or 4.16 per cent. Heated for another hour at 160°, the acid showed no further loss of weight. The calculated loss for  $H_2NC_6H_3\langle{}^{COOH}_{SO_2OH}$ + 0.5 H_2O is 0.0060 gram, or 3.98 per cent. Of a sample of the acid which had been previously heated to constant weight at 150° to 170°, 0.217 gram required 19.95 cc. 0.1 N sodium hydroxide; calculated, 20 cc. *o*-Amino-*p*-sulphobenzoic acid, therefore, contains half a molecule of water of crystallization. When the hydrated acid is heated in a melting-point tube to 240°, it darkens somewhat but fails to melt at 250°. According to Hart, dilute solutions of *o*-amino-*p*-sulphobenzoic acid and its barium salt show a beautiful blue fluorescence. As compared with sulphate of quinine and aesculin, the fluorescence both of this acid and of the aminobenzoic sulphinide is more of a rich bluish purple than a pure blue. This fluorescence is by no means confined to solutions of the free acid and its barium salt but, as one would naturally expect, is probably shown by dilute solutions of all salts of the acid, certainly by all which have been examined up to this time, *viz.*, by the sodium, potassium, ammonium, calcium, barium, lead, magnesium, zinc, manganese, and silver salts. It seems reasonably safe to conclude, therefore, that all of the salts of this acid with a colorless base show a bluish purple fluorescence at great dilutions.

It is also interesting to note in this connection that in ordinary white light, at least, the intensity of the fluorescence of *o*-amino-*p*-sulphobenzoic acid is, within wide limits, inversely proportional to the concentration of its aqueous solutions.

Thus a solution containing 15.48 grams of the acid per liter was found to exhibit, in diffused light at ordinary room temperature, only a slight fluorescence which was by no means comparable in intensity with that of a solution containing only 0.01548 gram per liter. In other words, a solution containing 0.01548 gram of the acid per liter exhibits a far more intense fluorescence than a solution containing a thousand times this quantity of the substance. It has also been found that a 0.001 gram-molecular solution of the acid is decidedly more fluorescent than a 0.01 gram-molecular solution. On the other hand, while a 0.0001 gram-molecular solution of the acid still exhibited a perceptible fluorescence it was decidedly less fluorescent than a 0.001 gram-molecular solution, indicating that there is a limit to the increase in fluorescence by dilution.

The effect of dilution on the intensity of the fluorescence of this compound is so marked, however, that the best way to exhibit its fluorescence in diffused daylight is to drop a few drops of a saturated solution of the acid into a large volume of water, when the path of the more concentrated solution is marked by a very deep and vivid bluish purple fluorescence. It has been observed also that heat diminishes the intensity of the fluorescence of solutions of *o*-amino-*p*-sulphobenzoic acid and its salts.

The fact that the fluorescence of *p*-aminobenzoic sulphinide in ultraviolet light is destroyed by concentrated hydrochloric acid naturally led me to study the effect of strong acids and alkalies on the fluorescence of *o*-amino-*p*-sulphobenzoic acid. This effect is shown in the following series of experiments: A solution (*1*) was prepared containing 0.0226 gram of the *o*-amino-*p*-sulphobenzoic acid in 50 cc. of water. Four tubes were then prepared containing 2 cc. of solution (*1*) and 1 cc. of water or a solution of acid or alkali. The intensity of the fluorescence of these several solutions was then determined by direct comparison with one another, with results as indicated below.

No. of tubes.	Substance.	Intensity of fluorescence.
1	1 cc. water	Strong bluish purple fluorescence
2	1 cc. 1 N hydrochloric acid	Colorless, without fluorescence
3	1 cc. 1 N sodium hydroxide	Colorless, without fluorescence
4	3 cc. water	Colorless, without fluorescence[1]
5	1 cc. 1 N acetic acid	Strong bluish purple fluorescence

In another series of observations, 2 cc. of a 0.01 gram-molecular solution of the amino acid was employed with water, hydrochloric, oxalic, *p*-nitrotoluenesulphonic and acetic acids. The following results were obtained.

No. of tubes	Substance.	Intensity of fluorescence.
1	1 cc. water	Strong bluish purple fluorescence
2	1 cc. 1 N hydrochloric acid	Colorless, no fluorescence
3	1 cc. 1 N oxalic acid	Very slightly fluorescent
4	1 cc. 1 N acetic acid	Strong bluish purple fluorescence
5	1 cc. 1 N nitrotoluenesulphonic acid	Colorless, no fluorescence
6	0.1 cc. 1 N hydrochloric acid	Fluorescent, less than (1)
7	0.1 cc. 1 N oxalic acid	More fluorescent than (6)

[1] Tube 4 contained only distilled water for purposes of comparison.

In another series of experiments, 2 cc. of a 0.01 gram-molecular solution of the amino acid were brought together with 2 cc. of the solutions indicated below and the mixed solutions made up to a total volume of 25 cc. with distilled water. They were then compared as to fluorescence with the following results:

No. of tubes.	Substance.	Intensity of fluorescence.
1	2 cc. water	Strongly fluorescent
2	2 cc. cane sugar (gram-molecular)	Strongly fluorescent
3	2 cc. sodium chloride (gram-molecular)	Strongly fluorescent
4	2 cc. hydrochloric acid (gram-molecular)	Only trace of fluorescence

It is evident, therefore, that the fluorescence of aqueous solutions of *o*-amino-*p*-sulphobenzoic acid is destroyed by strong acids and alkalies—the power to effect this change being roughly proportioned, at least, to the degree of ionization of the acid or base. That the depression of the fluorescence is due to hydrogen and hydroxyl ions is indicated by the fact that cane sugar and common salt have no influence on the intensity of the fluorescence exhibited by such solutions. The intensity of the fluorescence of dilute solutions of the amino acid has also been found to depend on the concentration of all of the substances concerned; for example, if a solution containing 2 cc. 0.01 gram-molecular amino acid and 1 cc. 1 N hydrochloric acid at a total dilution of 3 cc., and which is not fluorescent, is largely diluted with water, the solution again becomes fluorescent and more hydrochloric acid must be added in order to destroy the fluorescence. The effect of dilution on the power of hydrochloric acid to depress the fluorescence of aqueous solutions of the amino acid is shown by the results of the following observations:

Five tubes were prepared and numbered (1), (2), (3), (4) and (5). All contained 2 cc. 0.01 gram-molecular amino acid, in addition to which (1) contained 2 cc. of water, (2) 2 cc. 0.01 N, (3) 2 cc. 0.1 N, (4) 2 cc. 1 N hydrochloric acid, and

(5) 2 cc. 1 N acetic acid. Tubes (1) and (5) showed a strong purplish blue fluorescence, tube (4) only a trace of fluorescence, and tubes (2) and (3) a diminished fluorescence as compared with (1), the diminution being greater in (3) than in (2). In other words, the intensity of fluorescence in these tubes decreased in the order (5) = (1) > (2) > (3) > (4). In still another set of observations, intended to show the effect of hydrochloric acid and also that of dilution on the fluorescence, a set of tubes was prepared and numbered the same as in the above series, the only difference being that the total volume in each case was made up to 25 cc. with distilled water. In this series of observations (1) was found to be strongly fluorescent, (2) less fluorescent than (1), (3) less fluorescent than (1) and (2), and (4) only slightly fluorescent, less than any of the other tubes. In this series of experiments (4) was more strongly fluorescent than (4) in the former series and yet the same amounts of amino acid and hydrochloric acid were present in both, the difference being that the concentration of the two substances had been decreased 6.25 times in the last set of observations. In other words the actual concentration of the hydrochloric acid in (4) in the former series of observations was 0.5 N, whereas in the last series it was 0.08 N.

The effect of sodium hydroxide on the fluorescence of the amino acid is shown in the following table.

No. of tubes.	Amino acid (0.01 gram-molecular).	Other substances.	Degree of fluorescence.
1	2 cc.	23 cc. water	Strongly fluorescent
2	2 cc.	2 cc. 0.01 N NaOH	Slightly less than (1)
3	2 cc.	2 cc. 0.02 N NaOH	Distinctly less than (1) or (2)
4	2 cc.	2 cc. 0.1 N NaOH	Much less than (3)
5	2 cc.	2 cc. 1 N NaOH	Trace of fluorescence, less than (1), (2), (3) or (4)
6	None	25 cc. water	No fluorescence

Total volume in all tubes, 25 cc.

The effect of weak alkali in diminishing the intensity of the fluorescence of aqueous solutions of the amino acid is shown to best advantage at great dilutions. Thus, in a series of tubes containing the same quantities of amino acid and sodium hydroxide as in the foregoing, but at a total dilution of 100 cc., a very marked diminution in the degree of fluorescence was caused by 2 cc. of 0.02 and 0.01 N caustic soda. At the greater dilution (100 cc.), however, more sodium hydroxide is required to cause the complete disappearance of the fluorescence than at the greater concentration, *viz.*, 25 cc. This is due to the fact, already pointed out, that within very wide limits the intensity of the fluorescence of aqueous solutions of the amino acid increases with dilution. Whether, therefore, a solution of the amino acid will fluoresce in the presence of hydrochloric acid or sodium hydroxide depends on the degree of dilution of the amino acid and on the concentration of the hydrogen or hydroxyl ions. The diminution in the concentration of the hydrogen ions, resulting from the dilution of aqueous solutions of the amino acid, may also enable us to explain the increase in fluorescence resulting from increasing the dilution of aqueous solutions of the acid.

The degree of fluorescence of the normal and acid salts of the amino acid have been compared with that of the acid itself, using 2 cc. of a 0.01 gram-molecular solution of the acid and the quantity of base required to form the normal and acid salt, at a total dilution of 4 cc. and 25 cc. In some cases weighed amounts of the amino acid were brought together with the several amounts of carbonate of the metal required to form the mono and di salt of the acid and the resulting solutions diluted to 0.01 gram-molecular. These were then compared with 0.01 gram-molecular solutions of the amino acid at a total dilution of 4 and 25 cc. Without entering into the details of all of these observations, it has been found in the case of the sodium, potassium, ammonium, calcium, barium and magnesium salts that the intensity of the fluorescence is independent of the nature of the base (provided it be colorless) and that solutions of the free amino acid and of the mono or acid salts are decidedly more fluorescent than those of the di or neutral salts. In all cases, also, the fluorescence of solutions of the acid salts was somewhat more intense than that of solutions of the free acid at the same dilution, although the differences in degree of fluorescence were in no case so marked as those obtaining for the free acid or acid salt and the neutral salts.

The Disilver Salt of o-*Amino*-p-*sulphobenzoic Acid.*—With the view of preparing the di esters of the amino acid the disilver salt has been prepared and studied. In order to prepare it, weighed amounts of the amino acid were neutralized with the calculated amount of sodium carbonate and to the solution thus obtained was added the required amount of silver nitrate, dissolved in a small amount of water. When these operations are carried out at room temperature, the disilver salt is obtained in the form of an amorphous, curdy, light buff-colored precipitate. On gently warming the liquid containing the amorphous silver salt in suspension, the salt dissolves and almost instantly separates from the light brown solution, this time in the form of a distinctly crystalline, granular precipitate, which is considerably less soluble in water than the amorphous form.

Apparently, therefore, the disilver salt of *o*-amino-*p*-sulphobenzoic acid exists in two forms, one amorphous and curdy, the other crystalline. My attention was first drawn to this fact by reason of the following observations.

A weighed quantity of the amino acid was neutralized with sodium carbonate and precipitated with the calculated amount of silver nitrate. The amorphous precipitate thus obtained was at once filtered with the aid of the pump, and the amorphous mass spread out on filter paper to dry. In the course of a few minutes this tolerably dry material had greatly contracted in bulk and at the same time a large amount of mother liquor had exuded from the material, to such an extent, in fact, as to thoroughly wet the paper upon which the salt had been placed to dry. As the result of this change, the silver salt, which at first was perfectly smooth to the touch, had become gritty and when examined in strong light showed the luster and general appearance of a mass of small crystals.

A few additional observations on these two forms of the disilver salt of the amino acid are not without interest. Two solutions were prepared: (1) 0.226 gram of the hydrated amino acid and 0.106 gram sodium carbonate in 4 cc. of water; and (2) 0.3398 gram silver nitrate in 4 cc. of water. When these solutions were mixed in equal proportions by volume, a light buff-colored, curdy precipitate was formed. This precipitate tended to redissolve when the solutions were thoroughly mixed, and when gently warmed it did dissolve completely. On continuing to heat the solution, however, a heavy, crystalline, sandy-looking material was deposited which, under the microscope, was seen to consist of compact crystals, generally hexagonal in outline, with rounded edges. The large objects in the field of the microscope had the appearance of crystal aggregates. A microscopic slide was prepared by bringing together 1 drop of each of the solutions. Under a low power ($^2/_3$ in. objective) the precipitate had the appearance of a light brownish, translucent or transparent film. Under a higher power ($^1/_6$ in. objective) this film was seen to consist of a mass of very fine, rounded granules in a clearer and more transparent matrix, and of very irregular, much disintegrated and torn, finely granular, slightly brownish masses. After standing overnight, in a moist chamber to prevent evaporation, the amorphous film had disappeared and in its place crystals and crystal aggregates were to be seen. A similar change was noted in the silver salt which had been preserved in small test tubes, under its own mother liquor. At 27°.5,[1] therefore, the amorphous silver salt slowly changes into the crystalline modification and at higher temperatures, 60° to 100°, this change is practicably instantaneous.

It is evident, therefore, from these and many other observations of a similar nature, that the disilver salt of *o*-amino-*p*-sulphobenzoic acid exists in two forms, one amorphous and unstable at temperatures above 27°.5, the other crystalline and stable at 27°.5 and at higher temperatures. The amorphous variety of the silver salt has also been found to be much more soluble in water than the crystalline form.

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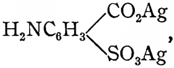
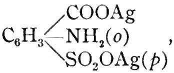
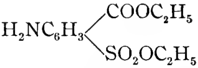
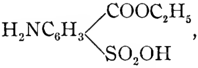
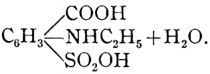
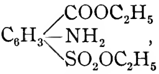
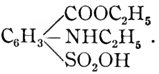
[1] By 27°.5 is not meant the transition temperature for this substance, but simply that at a temperature of 27°.5 and higher the amorphous variety of the silver salt becomes crystalline. The true transition temperature for these two forms of this silver salt, if such exists, has not as yet been determined.

Up to the present it has been found impossible to obtain the amorphous form in dry condition and, hence, no analysis of it has been attempted. There is nothing to indicate, however, that it is anything other than the disilver salt of the acid under consideration. Of the crystalline silver salt 0.1500 gram gave 0.0988 gram AgCl, corresponding to 49.6 per cent. of metallic silver; calculated for  $H_2NC_6H_3\left\langle\begin{matrix}CO_2Ag\\SO_3Ag\end{matrix}\right.$, 50.08 per cent. silver.

The yield of the crystalline form of the disilver salt depends obviously on the amounts of water employed in making up the solutions used in its preparation. The more concentrated the solutions used, the greater the yield of the silver salt. Thus, 5.942 grams of the silver salt were obtained by mixing together two solutions of (1) 5 grams of the anhydrous amino acid and 2.442 grams sodium carbonate in 50 cc. water and (2) 7.83 grams silver nitrate in 50 cc. water; whereas, when solutions (1) and (2) were prepared with half this quantity of water, *viz.*, 25 cc., 9.2 grams of the silver salt was obtained. In the former case the yield was only 60 per cent of the theoretical, whereas in the latter it was 91.7 per cent.

The Esters of o-*Amino*-p-*sulphobenzoic Acid.*—We have seen that all of the metallic salts of *o*-amino-*p*-sulphobenzoic acid which have thus far been prepared show the same fluorescence in their aqueous solutions as the acid itself. The question naturally suggests itself what fluorescence, if any, would be exhibited by the esters of this acid? So far as I am aware, there have been no attempts to prepare these compounds. With the view of obtaining the ethyl ester, the action of ethyl iodide on the disilver salt has been studied. It has been found that when ethyl iodide is added to the dry crystalline silver salt in the proportion of two molecular portions of the former to one of the latter, reaction occurs at once and silver iodide is formed with evolution of heat; and that in order to avoid loss of ethyl iodide by volatilization, it is necessary to work in closed vessels or under an inverted condenser. If the disilver salt has the constitution

 $C_6H_3\left\langle\begin{array}{l}COOAg\\ NH_2(o)\\ SO_2OAg(p)\end{array}\right.$, one would naturally expect a diethyl ester of the formula  $H_2NC_6H_3\left\langle\begin{array}{l}COOC_2H_5\\ SO_2OC_2H_5\end{array}\right.$ to be produced when two molecules of ethyl iodide are allowed to react with one molecule of the silver salt and that from this di ester an acid ester,  $H_2NC_6H_3\left\langle\begin{array}{l}COOC_2H_5\\ SO_2OH\end{array}\right.$, might easily be obtained.[1] As a matter of fact, however, the principal compound which I have thus far been able to obtain by the action of ethyl iodide on the disilver salt is a substance which, as nearly as I can judge at present, has the constitution  $C_6H_3\left\langle\begin{array}{l}COOH\\ NHC_2H_5\\ SO_2OH\end{array}\right. + H_2O$. This substance crystallizes from water in beautiful colorless, rhombic crystals, which melt with decomposition at 243°. In addition to this substance I once obtained a compound crystallizing from water in light, sulphur-yellow crystals, melting at 160°, and which was converted into the colorless rhombic compound by boiling its aqueous solution for some time. Unfortunately this substance was not obtained in sufficient amount for analysis. I am inclined to think, however, that it is a diethyl derivative of the amino acid, either the true di ester,  $C_6H_3\left\langle\begin{array}{l}COOC_2H_5\\ NH_2\\ SO_2OC_2H_5\end{array}\right.$, or a compound having the constitution  $C_6H_3\left\langle\begin{array}{l}COOC_2H_5\\ NHC_2H_5\\ SO_2OH\end{array}\right.$.

In the course of my attempts to prepare a true diethyl ester of *o*-amino-*p*-sulphobenzoic acid I have also obtained a barium salt, which seems to have the constitution

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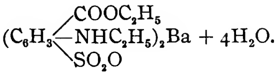
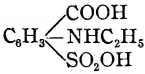
[1] For an account of the esters of certain sulphobenzoic acids see Kastle: THIS JOURNAL, **11**, 187–199 (1889).

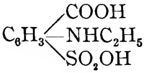


$$(C_6H_3\left<\begin{array}{l}COOC_2H_5\\ NHC_2H_5\\ SO_2O\end{array}\right.)_2Ba + 4H_2O.$$



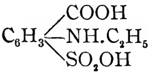
The Rhombic Acid, $C_6H_3\left<\begin{array}{l}COOH\\ NHC_2H_5\\ SO_2OH\end{array}\right. + H_2O$.—Up to the present, however, the rhombic compound obtained by the action of ethyl iodide on the disilver salt of *o*-amino-*p*-sulphobenzoic acid has chiefly engaged my attention, but even in my study of this substance I have been handicapped by reason of the fact that I have been able to obtain only poor yields of the substance and, hence, have had only small amounts at my disposal. In one experiment on the preparation of the rhombic acid 9 cc. of ethyl iodide were added to 18.5 grams of the dry, crystalline disilver salt and the flask containing these substances was at once connected with a reflux condenser. Reaction took place immediately, but in order to insure its completion the flask containing these substances was heated for an hour on the water bath, at the end of which time the excess of ethyl iodide was distilled off. The residue was then boiled with 50 cc. of water and filtered to remove silver iodide. During the extraction with boiling water it was observed that considerable effervescence occurred, due perhaps to the rapid formation and evaporation of alcohol or ethyl ether resulting from the decomposition of the normal ester. On cooling and on gradually evaporating in the air, the coffee-colored filtrate continued to yield successive crops of the rhombic compound in small amounts. In no case, however, have I been able to obtain anything approaching a theoretical yield of this substance. The rhombic acid was purified by recrystallization from hot water, the best results being obtained by evaporating its aqueous solutions until a few crystals began to appear on the surface of the solution. When such solutions are allowed to cool spontaneously in the air, the compound is obtained in the form of small, colorless crystals, which under the low power of the microscope are seen to consist of perfect rhombs. When shown some of these crystals, under the microscope, one of the chemists here said that they looked precisely like minute crystals of calcite. When first placed upon the tongue, the compound is almost tasteless. As it dissolves, however, it gives a mildly sour taste. Its aqueous solutions are acid to litmus and alkaline phenolphthalein. Its concentrated aqueous solutions show but little if any fluorescence. Its dilute solutions have a slight yellow color and show a beautiful pure blue fluorescence. On heating in a melting-point tube the compound begins to darken slightly at 206°, and at 243° it melts to a yellowish brown mass, with effervescence and partial decomposition. The compound is certainly a different chemical species from the *o*-amino-*p*-sulphobenzoic acid. On heating for one hour at 120° and for another hour at 140°, 0.3456 gram of the rhombic acid lost 0.0237 gram, or 6.85 per cent.

In a sulphur determination, by Liebig's method, 0.1673 gram of the compound gave 0.1463 gram $BaSO_4$, equivalent to 0.0201 gram of sulphur, or 12.01 per cent.; calculated for



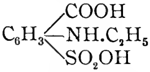
$$C_6H_3\begin{array}{l}\diagup COOH\\ -NHC_2H_5\\ \diagdown SO_2OH\end{array} + H_2O;\ H_2O = 6.84;\ S = 12.18.$$

On neutralizing a solution of the rhombic acid with 0.1 N caustic soda, using phenolphthalein as the indicator, 0.1000 gram of the compound required 7.2 cc.; calculated for

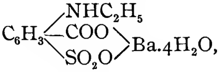
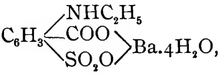


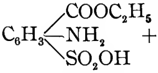
$$C_6H_3\begin{array}{l}\diagup COOH\\ -NH.C_2H_5\\ \diagdown SO_2OH\end{array} + 1H_2O,$$

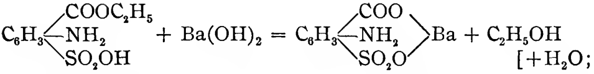
if both hydrogen ions are replaced by sodium, 7.6 cc. In another determination, 0.5000 gram of the acid required 37.41 cc. 0.1 N barium hydroxide; calculated for



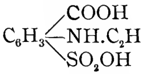
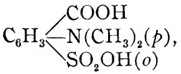
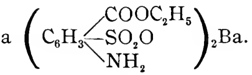
$$C_6H_3\begin{array}{l}\diagup COOH\\ -NH.C_2H_5\\ \diagdown SO_2OH\end{array} + 1H_2O,\ 38.00\ cc.$$

After neutralizing with 0.1 N barium hydroxide, the solution containing the barium salt was evaporated to small bulk and allowed to stand. Under these conditions the barium salt separated in white pearly plates, the crystal form of which was not very well defined. On drying in the air the barium salt was obtained in the form of a pearly, crystalline powder, which, on analysis, gave the following values for barium and water: 0.2000 gram of the air-dried salt gave on precipitation with sulphuric acid 0.1004 gram $BaSO_4$, equivalent to 0.0591 gram, or 29.55 per cent., Ba; or calculated on the basis of the anhydrous salt, 35.45 per cent. Ba; calculated for  $C_6H_3\left<\begin{array}{l}NHC_2H_5\\COO\\SO_2O\end{array}\right>Ba.4H_2O$, 30.35 per cent., and for the anhydrous salt, 36.10 per cent. Ba. On heating to 160° to 180° for 3 hours, 0.2009 gram of the salt lost 0.0335 gram in weight, equivalent to 16.67 per cent. of water; calculated for  $C_6H_3\left<\begin{array}{l}NHC_2H_5\\COO\\SO_2O\end{array}\right>Ba.4H_2O$, 15.90 per cent.

The mass left after heating to 180° was light yellowish brown in color, indicating that some little charring had occurred. This may account for the fact that the loss which the salt sustained on heating is a little more than the calculated for four molecules of water. It was thought at first that perhaps the rhombic acid, melting at 243°, was an acid ester of the formula  $C_6H_3\left<\begin{array}{l}COOC_2H_5\\NH_2\\SO_2OH\end{array}\right. + H_2O$. In fact, considering its method of preparation and the general tendency on the part of the di esters of the sulphobenzoic acids to form acid esters, everything would point to this formula for the compound. If now, barium hydroxide reacted with this, molecule to molecule, to form a neutral barium salt, it is necessary to suppose that the carboxylic ester part of the compound is instantaneously saponified by the barium hydroxide in the sense of this equation:



$$C_6H_3\left<\begin{array}{l}COOC_2H_5\\NH_2\\SO_2OH\end{array}\right. + Ba(OH)_2 = C_6H_3\left<\begin{array}{l}COO\\NH_2\\SO_2O\end{array}\right>Ba + C_2H_5OH\ [+H_2O;$$

in which event we should obtain the original *o*-amino-*p*-sulphobenzoic acid by the action of sulphuric acid on the barium salt. On the other hand, on evaporation, the filtrate obtained in the barium determination on this salt yielded the original rhombic acid from which the barium salt had been prepared by neutralization with barium hydroxide, *viz.*,  $C_6H_3\begin{array}{l}\diagup COOH\\ -NH.C_2H_5\\ \diagdown SO_2OH\end{array} + H_2O$, as determined by its melting point and other physical characteristics. In the formation of the rhombic acid, therefore, it is necessary to assume a migration of an ethyl group from either the carboxyl or sulphoxyl group to the amino part of the compound or a migration of the silver atoms to the amino part of the compound in the preparation of the disilver salt. In fact, the peculiar behavior of the silver salt in passing from an amorphous to a crystalline form naturally suggests some such molecular rearrangement; and certainly everything that is now known concerning the rhombic acid points to its being the monohydrate of *o*-ethylamino-*p*-sulphobenzoic acid. It is of interest to note in this connection that in his attempts to prepare the dimethyl ester of *p*-amino-*o*-sulphobenzoic acid, by the action of methyl iodide on the silver salt of this acid, Hedrick[1] obtained a dimethylaminosulphobenzoic acid,  $C_6H_3\begin{array}{l}\diagup COOH\\ -N(CH_3)_2(p),\\ \diagdown SO_2OH(o)\end{array}$ in which the two methyl groups are in combination with the nitrogen. On the other hand, by the action of ethyl iodide on the silver salt of the *p*-aminosulphobenzoic acid and subsequent neutralization of the product with barium carbonate he obtained a barium salt to which he assigned the formula  $\left(C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2O\\ \diagdown NH_2\end{array}\right)_2Ba$. It is evident, therefore, that the esterification of the aminosulphobenzoic acids is a process which will well repay further investigation. This investigation is now under way.

Like the parent acid, the ethyl derivative of *o*-amino-*p*-sulphobenzoic acid is fluorescent in its dilute aqueous solutions. These solutions have a faint yellowish color and ex-

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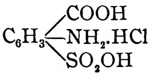
[1] THIS JOURNAL, **9**, 413–414 (1887).

hibit a strong, pure blue fluorescence, instead of the more purplish-blue fluorescence of the amino acid. In this connection it is interesting to note that in certain instances, at least, the introduction of ethyl groups into red dyestuffs changes their color to blue. The effect of introducing an ethyl group into *o*-amino-*p*-sulphobenzoic acid certainly has the effect of rendering the fluorescence more blue. Like the original amino acid, the ethyl derivative exhibits but little if any fluorescence in concentrated aqueous solutions. At great dilution, however, the fluorescence is very intense. The barium salt of the ethyl acid also shows the same fluorescence as the ethyl acid itself.

Attempts to prepare the benzoyl derivative of *o*-amino-*p*-sulphobenzoic acid have been without success—the only products resulting from the benzoylation being the unchanged amino acid and benzoic acid. These experiments were carried out, however, before I was aware that the amino acid contained water of crystallization and it is more than likely that the presence of water in the compound prevented the formation of the benzoyl derivative.

On the other hand, Hedrick[1] also failed to obtain the benzoyl derivative of *p*-amino-*o*-sulphobenzoic acid, which is anhydrous, so that the failure to obtain the benzoyl derivative in the present case may not be due to the presence of water in the molecule, but to some protection afforded the amino group by the other groups present in the molecule. If there is an actual shifting of the silver atoms from the acidic groups of the compound to the nitrogen, then it ought to be possible to obtain the benzoyl derivative by the action of benzoyl chloride on the silver salt. This point will be further investigated.

Attempts to prepare salts of the amino acid of the type of the hydrochloride  $C_6H_3\begin{cases} COOH \\ NH_2.HCl \\ SO_2OH \end{cases}$ have likewise resulted in failure, possibly for the reason that the hydrated amino

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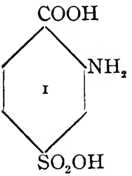
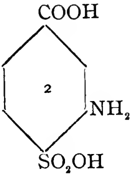
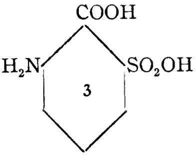
[1] *Ibid.*, 414.

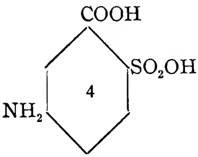
acid was also employed in these experiments. Further efforts will, therefore, be made to obtain salts of the substituted ammonium type by working with the anhydrous acid.

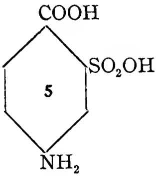
As is well known, there are, according to our present views respecting isomerism in the benzene series, ten isomeric monaminosulphobenzoic acids. These have the following formulas:

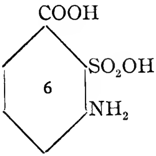


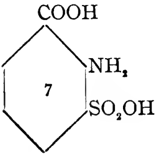


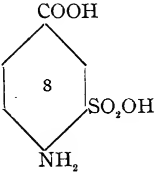


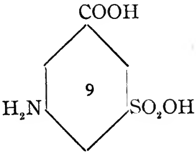


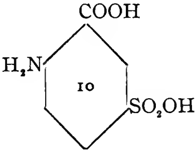




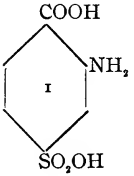




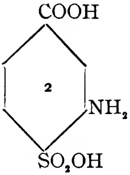




According to Richter eight of the compounds given in the literature as having the composition $C_7H_7O_5NS$ are aminosulphobenzoic acids. So far as I have been able to ascertain, however, and in this search I have been aided by Mr. McDermott of the Hygienic Laboratory, Washington, D. C., to whom my thanks are due, only five are described in the literature at present accessible to me. These are:



1



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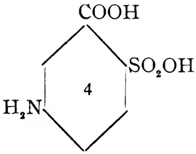

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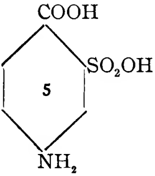

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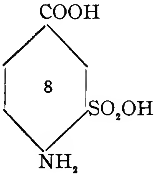

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It is interesting to note that except in the case of (1) and (2), nothing is said as to the fluorescence of any of these five acids. The compound (1), of course, is the acid here under consideration and is markedly fluorescent. In the case of (2), Hart described the fluorescence of dilute solutions of its barium salt, but makes no mention of the fluorescence of the acid itself. From my own observations on the fluorescence of the *o*-amino-*p*-sulphobenzoic acid, and its salts, it appears more than likely that Hart's acid (2) will itself be found to be fluorescent. It is also certain that in ordinary white light neither the *p*-amino-*o*-sulphobenzoic acid (5) itself nor its salts are fluorescent. It is also interesting to note that in the two aminosulphobenzoic acids in which fluorescence has been observed, *viz.*, (1) and (2), the amino group is in juxtaposition to one of the other groups in the molecule and not further removed than the meta position from the second acidic group. Furthermore, if Hart's observations are correct, acid (1) is more strongly fluorescent than acid (2). In the former the amino group is ortho to the carboxyl and meta to the sulphonic acid group, whereas in the latter the position of the amino group with respect to the other two groups is reversed. If now the relative position of the amino group with regard to the carboxyl and sulphonic groups in this series of compounds is the sole determining factor in the fluorescence or nonfluorescence of the aminosulphobenzoic acids, then we would expect to find acid (7) to be the most strongly fluorescent of any of these compounds. Acids (3) and (10) would also probably exhibit fluorescence, whereas acids (4), (5), (8) and (9) should exhibit no fluorescence. As a matter of fact, while acids (4), (5) and (8) are all known, nothing has been said by any author to indicate that either of them is fluorescent. Acid (6) presents such peculiarities with regard to the relative position of the amino group with respect to the carboxyl and sulphonic groups that at present nothing can be said as to the probability of its showing fluorescence.

The whole problem of the relation of constitution to fluorescence in the case of these aminosulphobenzoic acids is of great chemical interest and is such as to warrant an exhaustive investigation. Indeed, it would seem that a better idea of the influence of constitution on the phenomenon of fluorescence could be obtained from an intensive study of a comparatively small series of closely-related compounds, such as these aminosulphobenzoic acids, than we could ever hope to obtain from investigations covering such a wide range of chemical substances as are ordinarily included in investigations of this kind. I hope, therefore, to continue this investigation as rapidly as the time at my disposal and the resources of my laboratory will permit.

University of Virginia,
October, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXVII.—RESEARCHES ON PURINES: ON AN ISOMER OF XANTHINE; 2,8-DIOXYPURINE.

By Carl O. Johns.

[SECOND PAPER.[1]]

Two of the three isomers of dioxypurine required by theory have been described in chemical literature, namely, xanthine or 2,6-dioxypurine (IV) and 6,8-dioxypurine (VI). The synthesis and properties of 2,8-dioxypurine (V) are described in this paper.

The first known and most inportant of these dioxypurines is xanthine. This compound was described in the year 1817 by Marcet[2] who isolated it from urinary calculi. The structure of xanthine remained unknown for a long time. Medicus[3] proposed the formula of 2,6-dioxypurine (IV) as probably representing its constitution. From the results of his first investigations in this series, Emil Fischer was led to believe that xanthine[4] was 2,8-dioxypurine (V) and this formula was accepted for many years. By his later investigations, Fischer showed that xanthine[5] is 2,6-dioxypurine (IV). Fischer and Ach[6] have prepared 6,8-dioxypurine (VI). This compound is considerably more soluble than xanthine in hot water. Moreover, xanthine gives the murexide reaction while 6,8-dioxypurine does not. The writer has obtained 2,8-dioxypurine (V) by heating a mixture of urea and 2-oxy-5,6-diaminopyrimidine at 180°–190°. This is the method employed by Gabriel and Colman[7] to obtain purines from diaminopyrimidines.

2,8-Dioxypurine resembles xanthine in many respects. It gives a strong murexide reaction. When carbon dioxide

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[1] The first paper of this series appeared in This Journal, **41**, 58 (1909).

[2] An Essay on the Chemical History and Medical Treatment of Calcal Disorders. London, 1817.

[3] Ann. Chem. (Liebig), **175**, 230 (1875).

[4] *Ibid.*, (Liebig), **215**, 313 (1882).

[5] Ber. d. chem. Ges., **30**, 549 (1897).

[6] *Ibid.*, Ges., **30**, 2218 (1897).

[7] *Ibid.*, Ges., **34**, 1247 (1901).

is passed into a potassium hydroxide solution of the base, the free base is precipitated. Its hydrochloride is analogous to that of xanthine. Solutions of the base in mineral acids give a precipitate of the free base when poured into water. It is slightly more soluble than xanthine in hot water.

The sodium and potassium salts of 2,8-dioxypurine are but moderately soluble in cold water and are easily prepared. The sodium salt is the most characteristic of the two, forming stout prisms that contain 4 molecules of water. The sodium salt of xanthine contains but 1 molecule of water.

If 2,8-dioxypurine were formed in the hydrolysis of nucleoproteids or nucleic acids, it could easily be mistaken for xanthine. It can be distinguished from xanthine by preparing the sodium salt. This can be done with less than 0.5 gram of the base.

The greatest difficulty encountered in these experiments was in the preparation of 2-oxy-5,6-diaminopyrimidine[1] (II). Attempts to prepare it in quantity by reducing nitrocytosine (I) with aluminium amalgam resulted chiefly in the formation of black decomposition products. After various reducing agents had been tried without success, it was found that the use of ferrous hydroxide gave a yield of more than 60 per cent. of the pure crystallized diaminopyrimidine. It is probable that other nitropyrimidines can be successfully reduced by this method.

2-Oxy-5,6-diaminopyrimidine is more stable than we were led to believe in our former paper.[2] The presence of a large quantity of decomposition products made it appear that the pyrimidine was extremely unstable. Its aqueous solution can be evaporated under atmospheric pressure without marked decomposition. The base has also been found to give well-crystallized salts with mineral acids. The solution which we used in our previous work was probably too dilute as we did not obtain any salts at that time.

When 2-oxy-5,6-diaminopyrimidine is heated in a sealed tube with 20 per cent. sulphuric acid at 140°–150° it is readily converted into isobarbituric acid (III). This makes it im-

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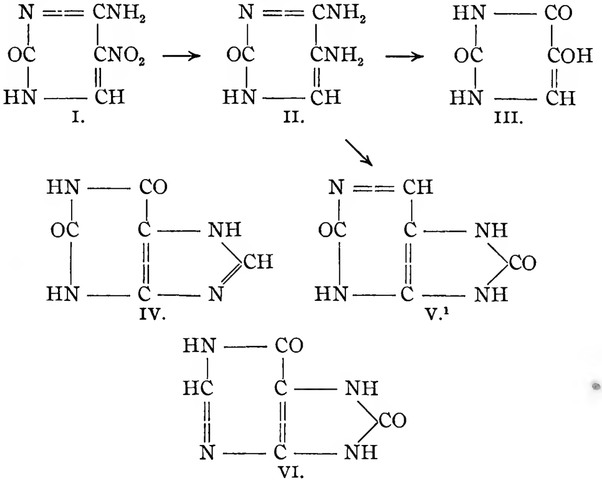
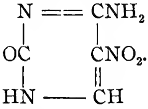
[1] Johnson, Johns and Heyl: THIS JOURNAL, **36**, 170 (1906).

[2] *Loc. cit.*

probable that 2-oxy-5,6-diaminopyrimidine will be found in the hydrolysis of nucleic acids, because if it were formed as a cleavage product it would readily be changed to isobarbituric acid These researches will be continued.


I. II. III. IV. V.[1] VI.

EXPERIMENTAL PART.

Nitrocytosine,[1] .—The nitrocytosine used in

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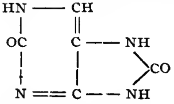
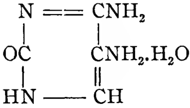
[1] The writer has used the formula proposed by Fischer (*Untersuchungen in der Puringruppe*, p. 19) to represent the structure of 2,8-dioxy purine. If written in its tautomeric form this would be  which would, perhaps, show more clearly the relationship between 2-oxy-5,6-diaminopyrimidine (II) and 2,8-dioxypurine.

[2] Wheeler and Johnson: THIS JOURNAL, **31**, 591 (1904). Johnson, Johns and Heyl: *Ibid.*, **36**, 166 (1906).

these experiments was made from synthetic cytosine.[1] A quantitative yield was obtained as follows: Ten grams of dry cytosine were dissolved in 20 cc. of cold concentrated sulphuric acid, and 10 grams of nitric acid (sp. gr. 1.5) were gradually added. Heat was evolved and in some cases it became necessary to cool the mixture. After standing for fifteen minutes the resulting solution was poured into 200 cc. of cold water and the acids were neutralized with ammonia. The nitrocytosine separated rapidly and was filtered off and washed as soon as the mother liquor had become cold. The nitrocytosine thus obtained was almost white.

2-Oxy-5,6-diaminopyrimidine,[2]  —Eight grams of pulverized nitrocytosine were dissolved in 200 cc. of concentrated ammonia. To this was added a solution of 96 grams of crystallized ferrous sulphate in 300 cc. of water. When the two solutions were mixed there was a marked rise in temperature. When the mixture had stood at room temperature overnight, the sulphuric acid was precipitated by adding a solution of 112 grams of crystallized barium hydroxide in 200 cc. of hot water. The mixture was then heated for a half hour on the steam bath and carbon dioxide was passed in to remove a slight excess of baryta. After filtering the hot solution by suction, the filtrate was evaporated in an open dish on the steam bath until about 100 cc. remained. This was filtered to remove a slight precipitate. Slender, colorless prisms were formed on cooling the filtrate rapidly, but when cooled slowly, stout prisms were obtained, some of which were two cm. long. A small quantity of amorphous material was usually associated with the crystals. This was easily dissolved before filtering by the addition of a few drops of ammonia. The yield of pure hydrous crystals was 65 per cent. of the calculated.

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[1] Wheeler and Johnson: THIS JOURNAL, **29**, 498 (1903).

[2] Johnson, Johns and Heyl: *Ibid.*, **36**, 179 (1906).

4.130 grams of substance lost 0.520 gram of H_2O at 120°.
0.5592 gram of substance lost 0.0692 gram of H_2O at 120°.

	Calculated for $C_4H_6ON_4H_2O$.	Found. I.	Found. II.
H_2O	12.50	12.59	12.37
N	38.18	...	38.54

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	44.05

The diaminopyrimidine was easily soluble in hot and sparingly soluble in cold water. It could be recrystallized without apparent decomposition although its aqueous solution darkened slowly on prolonged boiling.

Action of 20 Per Cent. Sulphuric Acid Heated under Pressure.—One gram of the crystallized diaminopyrimidine was dissolved in 20 cc. of 20 per cent. sulphuric acid and the solution was heated in a sealed tube at 140°–150° for three hours. The tube was cooled overnight. It contained 0.7 gram of precipitate which was composed of small balls of microscopic prisms. These were difficultly soluble in hot water but dissolved easily in dilute ammonia. The aqueous solution reduced an alkaline silver nitrate solution with the formation of a silver mirror. The substance was identified as isobarbituric acid, both amino groups having been substituted by hydroxyl.

	Calculated for $C_4H_4O_3N_2$.	Found.
N	21.87	22.26

The Hydrochloric Acid Salt, $C_4H_6ON_4.2HCl$.—One-half gram of the hydrous diaminopyrimidine was dissolved in 20 cc. of hot 10 per cent. hydrochloric acid. The salt was rather difficultly soluble in the hot acid and separated on cooling, in plates that formed laminated clusters. These did not lose weight at 110°.

0.1328 gram of substance gave 0.1911 gram of AgCl.

	Calculated for $C_4H_6ON_4.2HCl$.	Found.
Cl	35.68	35.57

The Sulphuric Acid Salt, $C_4H_6ON_4.H_2SO_4.H_2O$.—One-half gram of the hydrous base was dissolved in 10 cc. of hot 10 per cent. sulphuric acid and the solution was left at room temperature. Stout prisms separated. When cooled rapidly the solution gave needles or slender prisms. The deposit weighed 0.6 gram when dried over sulphuric acid.

0.3997 gram of substance lost 0.0265 gram of H_2O at 110°.

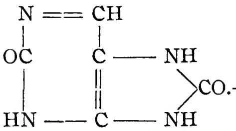
	Calculated for $C_4H_6ON_4.H_2SO_4.H_2O$.	Found.
H_2O	7.43	6.64

0.1212 gram of anhydrous substance gave 0.1212 gram of $BaSO_4$.

	Calculated for $C_4H_6ON_4.H_2SO_4$.	Found.
S	14.28	13.74

The Nitric Acid Salt, $C_4H_6ON_4.4HNO_3$.—One-half gram of hydrous base was dissolved in 7 cc. of hot 20 per cent. nitric acid. Crystals formed slowly but after standing in a test tube for 2 days the deposit weighed 0.8 gram. The crystals were stout colorless prisms and were anhydrous. They decomposed slowly when heated at 110°. Analyses of the air-dried crystals indicated that they were composed of 1 molecule of base to 4 molecules of nitric acid.

	Calculated for $C_4H_6ON_4.4HNO_3$.	Found.		
		I.	II.	III.
N	29.63	29.02	29.30	29.84



2,8-Dioxypurine,—Four and six-tenths grams of dried 2-oxy-5,6-diaminopyrimidine were mixed with 5 grams of urea and the mixture was ground to a fine powder in a mortar. This powder was then heated at 180°–190° in an oil bath for a half hour. The powder melted and gave off ammonia, leaving a hard cake. This was treated with hot dilute ammonia and gave a straw-colored solution. A trace of insoluble substance was filtered off. On acidifying the hot solution with acetic acid, and cooling, 5.1 grams of 2,8-dioxypurine were obtained. This was 92 per cent. of the theoretical yield. The purine was almost insoluble in cold water, and it required about 1100 cc. of boiling water to dissolve 1 gram. When precipitated from a hot ammoniacal solution by acetic acid the purine comes down as a white powder which is composed of extremely small microscopic prisms. When the purine was dissolved in hydrochloric acid to which a crystal of potassium chlorate was added and the resulting solution was evaporated carefully a yellow residue was obtained. When this residue was moistened with ammonia it turned purple, giving the murexide reaction. Analyses of the purine gave the following results:

0.1687 gram of substance gave 0.0437 gram of H_2O and 0.2471 gram of CO_2.

0.1517 gram of substance gave 0.0411 gram of H_2O and 0.2218 gram of CO_2.

	Calculated for $C_5H_4O_2N_4$.	Found. I.	II.
C	39.47	39.95	39.88
H	2.63	2.87	3.00
N	36.84	36.92	...

A solution of the sodium salt in water gave precipitates with silver nitrate, lead acetate, and mercuric chloride. Carbon dioxide precipitated the free base from its potassium hydroxide solution. A solution of the base in mineral acids gave a precipitate of free base when poured into water.

The Nitric Acid Salt, $C_5H_4O_2N_4.2HNO_3$.—This was obtained by dissolving 0.4 gram of 2,8-dioxypurine in 5 cc. of hot 20 per cent. nitric acid. On standing overnight the solution gave a deposit of short, stout prisms. The yield was 0.6 gram or 82 per cent. of the calculated.

	Calculated for $C_5H_4O_2N_4.2HNO_3$.	Found. I.	II.
N	30.21	30.00	30.41

The Hydrochloric Acid Salt, $C_5H_4O_2N_4.HCl$.—When the purine was mixed with hydrochloric acid, a hard crust formed, rendering the salt rather difficultly soluble. One-half gram of 2,8-dioxypurine was dissolved in 15 cc. of hot concentrated hydrochloric acid and the solution allowed to stand overnight. Small prisms with a lenticular outline separated. These weighed 0.3 gram.

0.1589 gram of substance gave 0.1166 gram of AgCl.

	Calculated for $C_5H_4O_2N_4.HCl$.	Found.
Cl	18.81	18.15

The Potassium Salt, $K.C_5H_3O_2N_4.2H_2O$.—This compound crystallized out rapidly when 0.5 gram of 2,8-dioxypurine was dissolved in 10 cc. of hot normal potassium hydroxide and the solution was cooled. The yield was 0.6 gram, or 80 per cent. of the calculated. The salt formed a bulky mass of needlelike crystals. It contained 2 molecules of water which it lost at 130°, but the anhydrous salt absorbed water slowly from the air until 2 molecules of water had been absorbed.

0.5080 gram of substance lost 0.0785 gram of H_2O at 130°.
0.5037 gram of substance lost 0.0759 gram of H_2O at 130°.
0.1172 gram of anhydrous substance gave 0.0533 gram of K_2SO_4.

	Calculated for $K.C_5H_3O_2N_4.2H_2O$.	Found. I.	II.
H_2O	15.92	15.45	15.07

	Calculated for $K.C_5H_3O_2N_4$.	Found.
K	20.52	20.42

The Sodium Salt, $Na.C_5H_3O_2N_4.4H_2O$.—One-half gram of 2,8-dioxypurine was dissolved in 5 cc. of hot normal sodium hydroxide. After the resulting solution had stood overnight, a compact mass of stout prisms was obtained. These weighed 0.5 gram, or 60 per cent. of the calculated. An attempt was made to dry the salt over sulphuric acid but it lost its luster and part of the water of crystallization. The air-dried salt contained 4 molecules of water.

0.4578 gram of substance lost 0.1320 gram of H_2O at 130°.
0.3825 gram of substance lost 0.1116 gram of H_2O at 130°.
0.1870 gram of anhydrous substance gave 0.0741 gram of Na_2SO_4.

	Calculated for $Na.C_5H_3O_2N_4.4H_2O$.	Found. I.	Found. II.
H_2O	29.26	28.84	29.18

	Calculated for $Na.C_5H_3O_2N_4$.	Found.
Na	13.21	12.85

The Ammonium Salt.—This was obtained as a mass of slender needles when 2,8-dioxypurine was recrystallized from ammonia. It was unstable when dried, losing ammonia rapidly.

NEW HAVEN, CONN.,
November 5, 1910.

REVIEWS.

RADIOCHEMISTRY. By A. T. CAMERON, M. A., B.Sc., Lecturer in Physiological Chemistry, University of Manitoba. London: J. M. Dent and Sons, Ltd. 1910. pp. viii + 174.

The scope of this little volume can be best seen from a few lines taken from the preface. "The title of this book has been chosen deliberately; the science of radioactivity has developed to such an extent as to make it justifiable and convenient to divide it. Here it is treated from a chemical standpoint; the physical side is introduced only so far as is necessary to explain the special experimental methods." The contents are: Historical Introduction; Radioactive Methods Illustrated by the Thorium Series of Elements; the Radiations from Radioactive Elements; Life of a Radioactive Element; Classification of the Radioactive Elements—Their Physical and Chemical Properties; Methods of Work with Radium Emanation and The Life Period of Radium; The Atomic Weight of the Emanations; Liquid and Solid Radium Emanation; the Chemical Effects Produced by the Radiations; The Production of Helium during Radioactive Changes and its Identity with the α Particle; Recent Attempts at Transmutation; Chemical Evidences of Transformation; Recent Results and Speculations; Radiogeology; The Medical Application of the Radiations. The author, having worked in this field to such good purpose with Ramsay, is eminently capable of dealing with the subject from the standpoint not of the compiler but of the investigator.

No chapters in the book will be read with more interest than those which deal with the transformation and transmutation of the chemical elements and it is interesting to all that the author distinguishes clearly between these two processes. When Ramsay first showed that helium is produced from the radium emanation, it was said, by some, that the dream of the alchemist had been realized, and that transmutation of one chemical element into another had been effected. A moment's thought showed that this was not true. Finding an unstable system in nature which spontaneously broke down, yielding other things, and among them an element, was very different from artificially producing one chemical element from another.

Cameron recognizes, very clearly, this difference and calls the first process "transformation" and the latter "transmutation" of the chemical elements. The work of Ramsay and Cameron on the production of lithium from copper is described in detail, and also the work of Mme. Curie and Mlle. Gleditsch in which negative results were obtained. Cameron sums up the facts thus: "The two series of experiments would appear to have been carried out in a perfectly parallel way; the only explanation that permits them to be homologated is that in those of Ramsay and Cameron, any lithium in the glass was undissolved by copper sulphate solution (as actually shown) unless emanation was present."

H. C. J.

CHEMISCH-OPTISCHE UNTERSUCHUNGEN. Von J. H. JELLETT. Übersetzt von L. FRANCK. Ostwald's Klassiker der Exakten Wissenschaften, No. 163. Herausgegeben von W. NERNST. Mit 6 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1908. pp. 83. Price, M. 1.60.

This number of the "Klassiker" is a translation of three papers from the Transactions of the Royal Irish Academy. Says Nernst: "This work of Jellett's contains apparently an entirely independent, and in many respects an original, development of the law of mass action, chiefly in its application to chemical statics. Yet, at the same time, the principles of chemical kinetics are clearly explained."

The priority in connection with the fundamental laws of chemical dynamics and equilibrium is usually accredited to the Norwegians, Guldberg and Waage. It seems that the work of Jellett takes its place with that of the above-named investigators. The convenient form and inexpensive character of the volumes published in "Ostwald's Klassiker" make this work readily accessible to all who are interested in this branch of science. H. C. J

DIE METHODEN DER MASSANALYSE. Zugleich völlig umgearbeitete 8. Auflage von FR. MOHR'S LEHRBUCH DER CHEMISCH-ANALYTISCHEN TITRIERMETHODE. Erste Abteilung. Von DR. H. BECKURTS, ordentlicher Professor und Vorstand der technischen Hochschule, Braunschweig. Unter Mitwirkung von DR. O. LÜNING. Mit 87 eingedruckten Abbildungen. Braunschweig: Vieweg und Sohn. 1910. pp. vii + 482. Price, M. 14.

In a prefatory note, the publishers state that the last edition of Mohr's "Titriermethode" which actually came from his pen was the fifth, published in 1877. Two later editions were issued (the last in 1896), which were revised by Professor Classen, the revision consisting mainly in the introduction of new methods without any extensive recasting of the remaining material. The purpose of the authors of the present edition has been to prepare what is practically a new work, taking Mohr's text-book as a model. They have intended to include all volumetric processes which have been proved to be of practical significance for a particular determination, and to discuss the practical application of each of these. They have, however, omitted material which occupied a considerable portion of Mohr's manual, namely the discussion of the application of volumetric processes in the more or less complete schemes of analysis of natural or artificial products, much of which dealt with gravimetric or gasometric methods not rigidly within the scope of a work on volumetric analysis.

The portion of the manual now published, and under review, includes a general discussion of the methods and apparatus employed in volumetric analysis, and the processes of alkalimetry and acidimetry (with an extended consideration of indicators), and the methods of iodimetry, chlorimetry and bromimetry.

There has been need of an authoritative work dealing with volumetric analysis which should bring the subject up to date. This volume seems to be such a treatise as is called for. The references indicate that the recent literature has received due attention (the text-books will always lag somewhat behind the latest utterances) and the theoretical discussions are modern in character. Any work which attempts to cover so wide a field must serve rather as an index to original sources of information than as an exponent of details. In this case the compilation appears to have been carefully done, and the volume may be heartily commended to the attention of all analysts.

The second division of the work is promised in the near future and its appearance is anticipated with interest.

H. P. TALBOT.

THE CHEMICAL ANALYSIS OF ROCKS. By HENRY S. WASHINGTON, PH.D. Second edition. New York: John Wiley and Sons. 1910. pp. xi + 200. Price, $2.

The new edition differs very little from the first.[1] The book has been somewhat enlarged by the introduction of new methods and by additional detail in the description of some of the older processes. The subject matter has been partly rearranged so that the directions for procedure more nearly parallel the actual laboratory work. The manual should be very useful to the chemist or petrologist with slight analytical training.

R. S. WILLIAMS.

SOILS AND MANURES. By J. ALLAN MURRAY, B.Sc. New York: D. Van Nostrand Company. pp. xiii + 354. Price, $2.00

This book deals with the origin, physical properties, chemistry and biology of soils, the principles of manuring and the various sources of plant food. It is of value to the student who desires to secure information concerning the principles of manure and soil fertility from the English point of view. It cannot, however, be recommended to those who are seeking information concerning American soils or American fertilizing practices. Matters of importance to an American are hardly mentioned and many things are discussed in detail which are of comparatively little importance in this country. Cotton and Indian corn, for example, are hardly mentioned at all. The expression of analyses of mixed fertilizers in terms of phosphates instead of phosphoric acid is not in accordance with our usage. Acid phosphate is extensively mixed with almost all kinds of material in this country and the cautions concerning its mixing and the statement that the only safe rule is not to mix phosphate with anything before applying it to the land appear peculiar to us.

G. S. FRAPS.

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[1] THIS JOURNAL, **33**, 435.

VOL. XLV. FEBRUARY, 1911. NO. 2.

AMERICAN
CHEMICAL JOURNAL

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

PART I. THE MANUFACTURE OF THE CELLS EMPLOYED IN THE MEASUREMENTS.

BY H. N. MORSE, W. W. HOLLAND, J. C. W. FRAZER AND B. MEARS.

In our last paper[2] upon the osmotic pressure of cane sugar solutions, an account was given of the then recent work at 20°, and a comparison was made of the results at this temperature with those which had previously been obtained at 0°, 5°, 10°, 15° and 25°. The experimental evidence which was then brought together, covering, at intervals of five degrees, the whole range of temperature from 0° to 25°, pointed unmistakably to the probable existence—for any given concentration of solution—of a constant ratio of osmotic to gas pressure; to the conclusion, in other words, that within these limits of temperature the temperature coefficient of osmotic pressure is, in the case of cane sugar, identical with that of gases.

The evidence was not of equal value throughout; for, during the progress of the work, the method had been steadily

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[1] The work upon osmotic pressure which has been in progress in this laboratory during the past 10 years is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257.

[2] THIS JOURNAL, **41**, 256.

improved, and one after another of the principal sources of error had been eliminated or reduced, so that each series of measurements was made under more satisfactory conditions than the one which preceded it. The progress in these respects had been so considerable that the results which were obtained at the lower temperatures might well be considered as crude and as much less trustworthy than those at the higher temperatures. Nevertheless, the results, even at 0°, 5° and 10°, were in fair quantitative accord as to the equality of the temperature coefficients of osmotic and gas pressures. Those at the higher temperatures, namely 15°, 20° and 25°, were strikingly so.

We did not consider the evidence which was offered sufficient to *prove* the equality of the coefficients in question, but rather as establishing a strong probability of it. Our attitude in the matter was expressed in the following words: "We do not permit ourselves, as yet, to entertain any *views* regarding the proper magnitude of osmotic pressure at any temperature; nevertheless we are prepared to state that all the best experimental evidence which we are now securing is tending strongly in the direction of establishing the substantial equivalence of the temperature coefficients of osmotic and gas pressure." The statement was intended, of course, to apply only within the field over which we had worked with care, namely, to cane sugar solutions ranging in concentration from 0.1 to 1.0 weight normal, and to temperatures between 0° and 25°.

In planning for the continuance of the work, it seemed best to devote our efforts principally to the further investigation of the relation of osmotic pressure to temperature, and to repeat, for that purpose, with all possible care, the work already done, rather than to bring other substances into the investigation or to experiment at temperatures above 25°. On the experimental side of osmotic pressure, the main problems for the present are: (1) what is its relation to temperature? and (2) what is its relation to concentration? To some extent, the investigation of both questions is necessarily simultaneous; but under present conditions the second may be kept somewhat in the background to the advantage of the first, for the reason that it is *easier* to determine, with a satisfactory degree of precision, the relation of pressure to temperature than its relation to concentration. We shall have occasion, at a later period, to discuss this matter in detail, but for the present it will suffice to recall, by way of explanation, the fact that in determining the temperature coefficient the unknown and indeterminable errors of the manometers are of much less importance than in determining the relation of pressure to concentration; since, in the former case, the pressures to be compared, *i. e.*, those of a given concentration at different temperatures, being approximately equal, errors of meniscus, of variable capillary depression, *etc.*, affect all the measurements in about an equal degree; whereas, in the second case, the pressures to be compared differ widely, and since the nitrogen gas occupies very different proportions of the manometer at different times, the local errors of the instrument affect the results unequally.

We have already nearly finished a repetition of the work at the six different temperatures mentioned above, and it is our purpose to describe, in this paper and in those which will follow it, the conditions under which it was carried out. A somewhat detailed account of the investigation will be given in order to enable others to judge justly what weight is to be attached to the results. As for ourselves, we are prepared to say that they appear *sufficiently to establish the equality of the temperature coefficients of osmotic and gas pressures.* We wish to emphasize again, however, the fact that the conclusion applies for the present only to cane sugar solutions between 0° and 25° and to concentrations of that substance which range from one-tenth to one gram-molecular weight dissolved in 1,000 grams of water. The ratio of osmotic to gas pressure has been found to remain (for any given concentration) very nearly constant up to 25°. What will be found at higher temperatures cannot yet be affirmed with certainty, but a few apparently reliable preliminary measurements, made on concentrated solutions at 30°, 40° and 50°, indicate that the ratio will be found to diminish at the higher temperatures, the decline beginning at some point between 25° and 30°. Any discussion at the present time of the cause of this apparent *dilution* of cane sugar solutions at temperatures above 25°—*i. e.*, whether it is due to a breaking down of the complexes of water molecules, to the dissociation of hydrates, or to some other change in molecular relations—would be premature owing to the meagerness of the established and pertinent facts in the case; and we mention it only because the hope seems to be already justified that the study of osmotic pressure at the higher temperatures, which will soon be undertaken, will throw much needed light upon the states of the solvent at different temperatures.

Before passing on to matters of method and procedure in the investigations of the past two years, we may be permitted to refer to certain facts which have doubtless contributed materially to the thoroughness of the work, and, we hope, to the trustworthiness of the results. It was realized quite early that the task we had undertaken was beset on all sides by great and unusual experimental difficulties; and that to so far master these that the results should be really convincing, more than the working lifetime of any one individual must be devoted to the undertaking. That we did not overestimate the magnitude of the difficulties to be encountered is shown by the fact that it has taken ten years of time, and—counted as the work of one man—over forty-five years of labor, merely to develop the method and to demonstrate to our satisfaction that the osmotic pressure of one substance obeys, within certain narrow limits of temperature, the law of Gay-Lussac for gases.

It also became apparent very early in the course of the investigation that this work—in which the success of an experiment depends upon the perfection of every one of a multitude of conditions, and in which failure is sure to follow the slightest neglect of any one of a great number of details—offers very unusual opportunities for self-deception as to the trustworthiness of the results.

The conviction that a condition of wariness and of distrustful caution on the part of the experimenter is indispensable has grown with our experience, until—after having made more than 3,000 quantitative experiments with osmotic cells—we are ready to affirm that no result as to the magnitude of osmotic pressure should be accepted until it has been confirmed by every practicable test, and, moreover, that every result which depends in any degree upon the *estimated* effects of hypothetical or unmeasured conditions should be unceremoniously rejected. By way of justifying this attitude, we will state, on the basis of our own experience, that, with imperfect methods and insufficient control of results, almost any view regarding the magnitude of osmotic pressure can be made exceedingly plausible.

In view of the magnitude of the difficulties to be overcome and especially the dangers of misinterpretation of results, it seemed to us that the value of the outcome would depend very largely upon our freedom from any preconceived notions as to what the results *ought* to be. Accordingly, we have endeavored to carry out the work without any personal convictions or beliefs in regard to the true osmotic pressure of solutions under any conditions of temperature or concentration, that is, without anything in mind which was to be *proved* or *disproved*.

The reasons for regarding the evidence brought together in our last paper as insufficient to establish beyond question the temperature coefficient of the osmotic pressure of cane sugar solutions between 0° and 25° may be summarized as follows:

1. The earlier series of measurements had been carried out with imperfect facilities for the automatic regulation of temperature, and fluctuations of bath temperature had occurred which we afterwards came to consider quite intolerable. The subject of "*thermometer effects*" in the cell, *i. e.*, the expansion and contraction of the cell contents, has frequently been mentioned in former papers as one of the serious difficulties in the way of the correct measurement of osmostic pressure, but we did not fully realize how great effects may be produced by even small fluctuations of temperature until we had succeeded by means of improvements in the cells

and the membranes in suppressing all dilution of the cell contents. After this had been accomplished, the observed fluctuations in pressure—after a maximum had been reached—could only be ascribed to irregularities of bath temperature, and to variations in atmospheric pressure. The effect of the latter, however, is relatively small except in the case of dilute solutions and its limits can be determined. In the course of the work at 20°, where there was no dilution of the cell contents which could be detected by the polariscope, it was found that a change of 0°.01 to 0°.02 in the bath temperature, unless distributed over a long period, was capable of producing distinct *thermometer effects*. This observation necessarily brought under suspicion the results in the earlier series, where the fluctuations in bath temperature had been much greater.

2. In all the six series of measurements, except that at 20°, there had been some occasional decrease in the concentration of the cell contents. In the first two series—those at 0° and 5°—a decrease had occurred in the majority of the experiments which amounted to an average of 1.73 and 1.45 per cent., respectively; while in the series at 10°, 15° and 25° it amounted to an average of 0.22, 0.10 and 0.20 per cent., respectively. Only the series at 20°, the last one, was faultless in respect to the dilution of the cell contents. As long as we were unable to suppress it altogether, we had endeavored to interpret this dilution or, rather, loss in rotation of the cell contents, and to estimate its effect upon the observed apparent osmotic pressure. But, unfortunately, the applicability of the corrections which were made depended on the correctness of our interpretation of the causes of the observed loss in rotation; and every explanation of this phenomenon which we have hitherto given has proved in the course of time to be either partly wrong or not wholly adequate. At first, we ascribed the loss in rotation mainly to an *inversion* of the cane sugar, but it subsequently appeared that the inversion which takes place in the closed cell is insignificant. One effect of correcting the loss in rotation as being due to inversion was to make it appear that the osmotic pressure of cane sugar solu-

tions is nearly proportional to concentration, whereas it afterwards became apparent that it runs nearly parallel with the freezing-point depressions. Later, the dilution of the cell contents was ascribed to certain conditions attending the closing and opening of the cells. But, since modifications of the cells which removed these conditions did not entirely suppress the dilution, it became certain that this explanation, though probably correct in the main, was not sufficient, and that the loss in rotation formerly observed was due, not to inversion, nor altogether to dilution at the time of closing and opening the cells, but to some extent to the imperfection of the membranes.

3. In the earlier work, the manometers had been filled with air. But it was found that in the instruments so filled the gas volume steadily diminished, and in time to an extent which had a sensible effect upon the apparent magnitude of the pressure. The changes in volume were ascertained from time to time, but probably not with the frequency which the importance of the matter demanded.

4. It is essential that the material used in determining a temperature coefficient shall be uniform in every particular. This is much more important, of course, than a high degree of purity. But the material which had been employed in the six series of measurements was not uniform throughout. The supply which had been used at 0°, 5°, 10°, 15° and 25° became exhausted while the work at 20° was in progress, and it was found that supposedly equivalent solutions of the old and the new materials did not give identical pressures.

Any one of the defects enumerated above would have afforded a sufficient justification for a repetition of the whole work; and, fortunately, we could undertake the task with a considerable degree of confidence in the value of the outcome, because the method of measuring osmotic pressure had already been developed and improved to a point where, in later work, we could nearly eliminate all of the faults which led us to distrust more or less the results of the earlier experiments. The cells and membranes had been so perfected that we were able to carry out the measurements of pressure without decrease in concentration in the cell contents. The facilities for the automatic regulation of temperatures had been improved until we could maintain, continuously for months, any desired temperature, with extreme variations not exceeding 0°.01 or 0°.02. Moreover, the manometers had all been recalibrated and refilled with nitrogen. As for the material for the solutions, which had failed at a critical time in the earlier investigation, we began with a supply of 75 kilograms of rock candy and purified it by repeated precipitations with alcohol, thus securing a supply of uniform material which was ample, not only for the work which is to be reported, but probably for any future experiments on the osmotic pressure of cane sugar solutions.

THE CELLS.

Much of the time during the past ten years has been spent in experimental work in the manufacture of cells. The first four years were devoted almost exclusively to that problem; and as the result of so much effort we had, at the end of this period, *two* cells with which we could measure osmotic pressure with some degree of confidence. At the present time we have about 30 cells which are suitable for the work. If these were lost, they could probably be replaced by an equal number of other cells in about two years' time. These statements will suffice to show that the problem of cell-making has been a very difficult one to solve. Certain qualities were found to be indispensable to the porous wall on which the membrane is deposited, and to secure all of these in one and the same product has cost much time and labor. Our earliest experience with porous cells was summarized in a paper published in 1905, as follows: "....it was supposed by the authors that, having solved in a satisfactory manner the problem of depositing the membranes, and having overcome, in a measure, the difficulties connected with the assembling of the different parts of the cell, they could proceed, without further delay, to the measurement of osmotic pressure. But it soon appeared that a third problem, the most difficult of all, remained to be dealt with, *i. e.*, the problem of the *porous* *wall.* The porous cups in which the high pressures referred to had been obtained were a part of a lot of 100 which were made for the authors at a pottery in a neighboring city. Out of this number 25 or 30 had been found to answer the requirements[1] moderately well, and it was not doubted that others equally good, or better, could be readily procured. In this we were greatly mistaken, for among the nearly 500 cells which were subsequently made for us at various potteries, *not one* was found suitable for the measurement of osmotic pressure. The entire year was spent in procuring and testing porous cells from different sources, but to very little purpose except to convince us that the problem of producing the cells must be worked out in the laboratory rather than at the pottery." The quotation above includes about all that we have hitherto published on the subject of cell making.

The cells produced at the potteries were defective in various ways, but principally in the particulars enumerated below:

1. They were all lacking in the strength necessary to withstand any considerable outward pressure. Only one of the few which proved at all serviceable survived a pressure of 30 atmospheres, while most of them cracked under pressures below 20 atmospheres.

2. All of them contained numerous "*air blisters*," which communicated with each other and with the interior surface of the porous wall in such ways as to give rise to the formation of a number of interior subsidiary membranes. Not infrequently, when the cell was broken for examination, as many as four or five of these minor membranes, often nearly parallel over a considerable area, were found in several localities; and it frequently happened also that the last of them was near, or even at, the exterior surface of the cell.

3. The cells obtained from the potters also lacked uniformity in respect to porosity. The same cell would often exhibit the greatest diversity in this respect. In some parts the structure would be as close as in porcelain, while in others it might be so open that the membrane was deposited nearly midway between the interior and exterior surfaces of the wall.

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[1] As we then understood them.

A microscopic study of thin sections of the cells in which membranes had been deposited revealed the fact that—excluding the peculiar and often fantastic effects produced by "*air blisters*"—the location of the membrane is determined by the porosity of the cell wall. The more open the texture is, the more deeply within the wall will the deposition occur; while with a certain degree of closeness in this respect, the deposition is upon the *interior surface* of the cell.

After a somewhat protracted study of the cells which were first furnished by the potters, we thought ourselves able to formulate quite definitely the more important qualities which are essential to a satisfactory cell wall, and to state, in a general way, how some of these may be secured. It was clear:

1. That the materials used in making the cells must be *thoroughly mixed* in order to secure uniform porosity and uniform strength.

2. That, in order to secure *great strength*, the maximum allowable proportion of binding material (feldspar, *etc.*) must be employed—that proportion, in fact, which is just insufficient to convert the baking cell into porcelain.

3. That all *air blisters* must be eliminated.

4. That the texture of the cell wall must be so fine and uniform as to compel the deposition of the membrane exclusively upon the inner surface of the cell.

The reason for the suppression of air blisters and for the deposition of the membrane on the *interior* surface of the cell will appear if we consider the inequalities in the concentration of the solution which must result from its location elsewhere, *i. e.*, *within* the cell wall. In the latter case, owing to the slowness of diffusion in the wall, the liquid in the neighborhood of the membrane will be permanently less concentrated than the main body of the solution; while if the discharge of the entering water is from a free surface, the conditions will be favorable to the maintenance of uniform concentration throughout the enclosed solution.

Our observations and conclusions were duly communicated to the potters who were interesting themselves in our behalf, and they assured us of their confidence in their ability to produce cells with all of the required characteristics. But their expectations were not realized, as we have already stated; for, of the several hundred cells which were subsequently made for us, not one proved serviceable for the measurement of osmotic pressure. In fact, the later products were inferior to the earlier ones. In most of them, some of the faults which were to be avoided were greatly aggravated. This was notably the case in the matter of uniformity of porosity. The reasons for the failures of the potters afterwards became clear to us when, in attempting to manufacture for ourselves, we fell, from time to time, into some of the errors which had prevented their success.

Having become convinced that the correct texture of porous wall for the measurement of osmotic pressure cannot be produced by the usual methods of the potter, we proposed to them to resort to certain new practices. But coöperation along these lines was declined on the ground that, to one experienced in the ways of clays, our plans were obviously futile. Hence, as a last resort, the problem of cell making was taken from the pottery into the laboratory. The processes by which we were able ultimately to produce cells with faultless wall texture are, on the whole, simple, and they can be adequately described in few words; but their development cost us several years of pioneer experimental work.

The problem to which attention was first given was that of securing *uniform porosity* combined with *great and uniform strength*. To this end, the washed clays from several sources were mixed with varying quantities of ground feldspar, and the mixtures were burned at different temperatures, either in a calibrated electric furnace or in a Seger experimental kiln. The products were altogether disappointing. They were, in fact, quite as uneven in respect to porosity and strength as the cells which had been obtained from the potters. Thinking that our failure might be due, in part, to the coarseness of the materials, the clays and the feldspar were subjected to elutriation, and the wet mixtures of the finer portions thus obtained were then passed repeatedly through silk bolting cloth having 16,000 holes to the square inch. The bolting process was followed by a long-continued churning of the mixture in water and, finally, by a most thorough kneading of the "putty." The results were still unsatisfactory, in that the porosity of the baked samples lacked the high degree of uniformity which is indispensable in the measurement of osmotic pressure. It was evident, moreover, on comparing our products with those of the potters, that we had been trying exactly what they had attempted except that they had omitted the elutriation and bolting processes to which we had resorted. We concluded that the necessary binding material *cannot* be successfully incorporated with the clays in the form of ground feldspar.

The final solution of the problem was easy and satisfactory. It occurred to us that perhaps sufficiently intimate admixtures might be obtained by bringing together two different clays, one of which is deficient in binding material while the other is overrich in that constituent. This was the plan which was adopted, and, with proper manipulation of the materials, it has never failed to give us products which, so far as we can discover, are perfect in respect to the uniformity of their porosity.

It remained to eradicate the air blisters which appear to be always present in cells made in the ordinary way, and to secure that degree of fineness of wall-texture which will cause the membrane to be deposited only upon the interior surface of the cell, and never sensibly within it. It is recalled here that, when the electrolytic deposition of the membrane is commenced, the cell wall which separates the two solutions is filled with water only, and that the position of the meeting place of the two kinds of ions is determined in great part by the size of the pores. If they are large, that is, if the wall-texture is what may be called an open one, the meeting place is within the wall, though always—in the absence of air blisters—somewhat nearer the interior than the exterior surface. If, on the other hand, the pores are small, the deposition occurs nearer the inner surface. Our problem was, of course, to produce a cell wall of such texture that the copper and ferrocyanide ions *must* meet just at the interior ends of the pores, that is, we were to produce a cell wall in which the pores were, not only of a *uniform* diameter, but at the same time *excessively small.* This is necessary, not alone for the purpose already alluded to, namely, that of securing uniform concentration throughout the solution, but also to give to the membrane the *support from the rear* which will enable it to withstand high pressures. A membrane which is deposited in large pores is easily ruptured, and no membrane, obviously, is superior to its weakest part.

We had suggested to the potters two plans for removing the air blisters, and for securing at the same time that extremely dense texture of cell wall which was thought to be essential. The first of these was to form the cell itself under high pressure, while the second was to form the wet clay into a cylinder under great pressure, and from this to turn out the cell upon the lathe. Both plans were pronounced impracticable by the potters. After many months of futile effort, we were forced to agree with them as to the first project, but the alternative plan—that of pressing the clay into a cylinder and cutting the cell from this upon the lathe—was finally developed to a successful issue. We will pass over our attempts to form the finished cells under pressure as something more instructive to ourselves than helpful to others, and proceed to describe the present method of making cells which, when successful, gives an entirely satisfactory product.

A. Treatment of the Clays.

A considerable number of clays, both American and foreign, were investigated with reference to their suitability for the manufacture of cells, and two were finally selected as being, in our judgment, superior to all others for the purpose. These were a fire clay from Mt. Savage, Maryland,[1] and a so-called ball clay from Edgar, Florida.

The Flordia clay had been washed before it came into our hands, but both varieties were treated in the same manner for the purpose of separating the finer from the coarser materials. The process is as follows: Three empty alcohol

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[1] The mine from which we obtained the fire clay has since become exhausted, and we are now searching for a substitute.

barrels, each with a spigot in the bung hole, are placed one above another, each of the upper two being set a little back of the one below it. The uppermost barrel is nearly filled with water, and into this is stirred about 3 kilograms of sifted clay. After standing quietly for three minutes, the spigot is opened and the contents of the upper half of the barrel are allowed to flow into the barrel below. The residue is removed and the barrel is recharged and again partially emptied, precisely as in the first instance. When the intermediate barrel is nearly full, its contents are likewise stirred and then allowed to settle for three minutes, after which the spigot is opened to allow the contents of the upper half of the barrel to run into the lowest receptacle. The material which collects in the last barrel is afterwards passed through silk bolting cloth having 16,000 holes to the square inch. The proportion of the original clay which is thus acquired for cell making is not very large. In one instance, where the weights of clay taken and of the final product were recorded, 500 pounds of the fire clay yielded 180 pounds of the product. In another case 200 pounds of the Edgar clay gave 75 pounds of the finer material.

It was found that the two clays, prepared as described above, mingle readily in all proportions, giving products which, when baked, are uniform in respect to texture and strength, and it was later ascertained that all the requirements of the situation are best met by mixing the two in about equal proportions by weight.

The process of mixing is as follows: (1) The two clays are mingled and repeatedly sifted in the dry state; (2) the mixture is then churned with water for several hours, after which (3) it is passed successively—without unnecessary interruption of the churning process—through two grades of bolting cloth, one of which has 16,000 and the other 26,000 holes to the square inch; (4) the material, after settling, is collected and drained upon a filter of bolting cloth resting upon one of paper; (5) it is then partially dried by heat; and, finally, (6) the mixture is kneaded upon a plate glass surface until, through evaporation of the excess of water, the "putty"

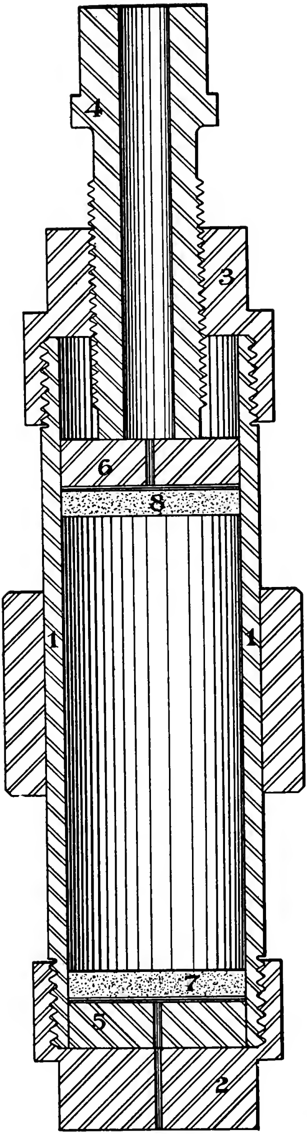

Fig. I.

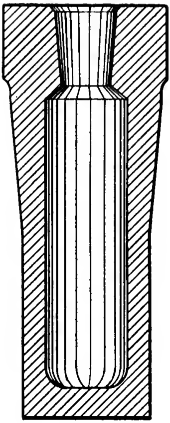

Fig. V.

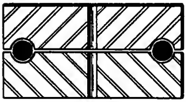

Fig. II.

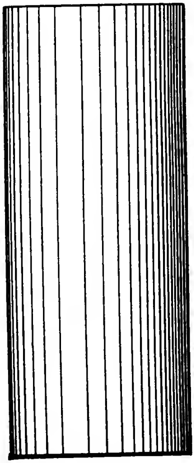

Fig. IV.

has attained the consistency which experience has shown to be best suited to pressing.

B. The Formation of the Cylinders.

A section of one of the steel presses in which the clay is compressed into cylinders is shown in Fig. I. The barrel (1) is threaded at both ends to receive the caps (2) and (3). The cap upon the lower end (2) is bored to permit the escape of the water which is squeezed out of the clay, while the cap upon the upper end (3) is bored and threaded internally to receive the hollow plug (4). The closely-fitting steel disks (5) and (6) are also bored to facilitate the escape of water. The disks (7) and (8) are of porous hard-burned clay, between which the clay is compressed by screwing down the plug (4) upon the steel disk (6). They may be replaced by disks of asbestos.

The upper steel disk (6) is less simple than it appears in the figure. In reality, two grooved disks, separated by hardened steel balls (bicycle balls), are used. The arrangement is shown in Fig. II. The upper half turns readily with the plug (4), which rests upon it, while the lower one remains stationary. If a single disk is employed, the clay is twisted in the direction of the screw thread, and the cell, when burned, exhibits upon its exterior surface a series of spirally arranged lines or depressions, as if the shrinkage of the clay in baking had not been entirely uniform.

Considerable difficulty was experienced at first in securing the correct temper for the steel disks, which should, of course, be equal to, but not much higher than that of the steel balls which separate them. If the disks are insufficiently tempered they are badly lacerated by the balls. On the other hand, if they are made too hard, they frequently crack under the great pressure to which the clay is subjected.

The device for compressing the clay is shown in Fig. III, without the framework which holds the various parts in their places. The press (1) containing the clay is secured between two flat bars of steel, a portion (2) of one of which is seen in the figure. The lower end of the shaft (3) is square in form like the upper end of the plug (4) of Fig. I, and the collar (4), which joins the two, has a square hole of the same diameter passing through it. A portion of two of the timbers of the framework is shown at (5) and (6). Through these the shaft (3) slides freely up or down, except so far as its motion is limited by the set-collar (7). The large wooden drum (8) is firmly attached to the shaft and around it is wound the steel wire cable. The loose iron pulleys (9, 10, 11) serve to guide the cable. The large pulley (12) is situated in the attic of the laboratory. The cable, after leaving (11), ascends vertically through the ceiling of the room, and, after passing over the pulley (12), it returns and is terminated by the heavy iron bar (13). Upon this are loaded as many of the cast-iron weights (14, 15) as may be required. At the floor, the weight (consisting of 14, 15, 16, *etc.*) enters a vertical passage which extends to the basement floor, fifty-five feet below. The detachable wrench (16) is provided with extensions and is employed to raise the weight and coil the cable about the drum.

When the press is to be packed with clay, it is placed in a vise, and the "putty" is introduced in small quantities. After each addition, the material is tamped down with a stick of hard wood and a hammer. The wrench is then applied and given a turn from time to time until the water nearly ceases to run. Finally, the press is placed in its position as shown in Fig. III, and the weight is released.

We have no invariable rule which is to be followed in pressing the clay. Usually, however, it is subjected for about 14 or 16 hours to an estimated total pressure of 200 tons. If a smaller pressure is used, the duration of the pressing period must be increased. The sole guide in the matter is the conduct of the product when it is cut into shape on the lathe. It must be neither *too wet* nor *too dry*.

C. The Cutting of the Cells.

The cutting of the cells is a very critical operation, which requires not only experience but also highly developed mechanical instincts. Very few, even of those who have had mechanical training, ever succeed in the undertaking. The ex-

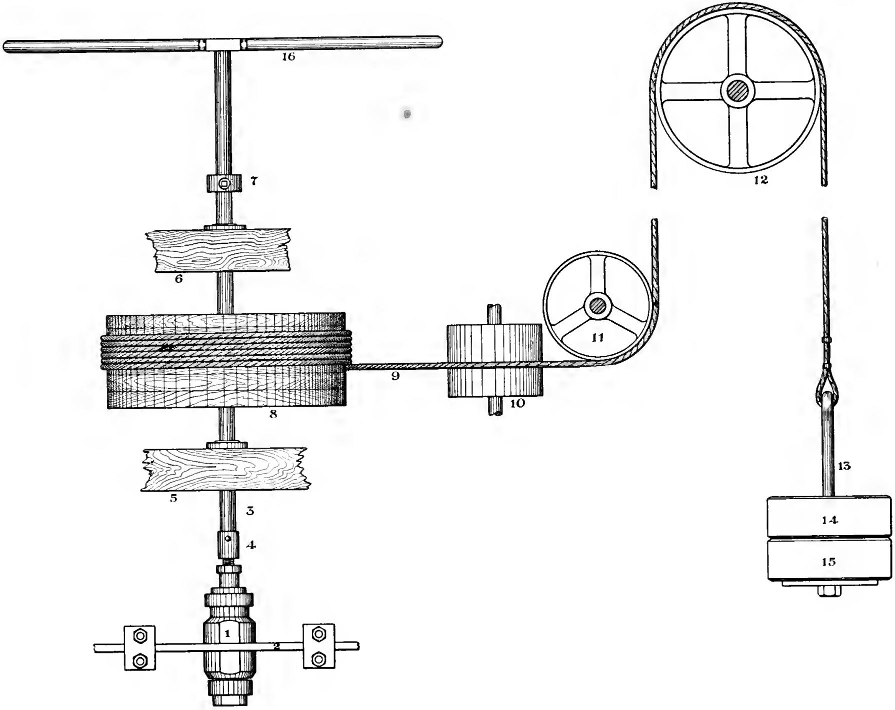

Fig. III.

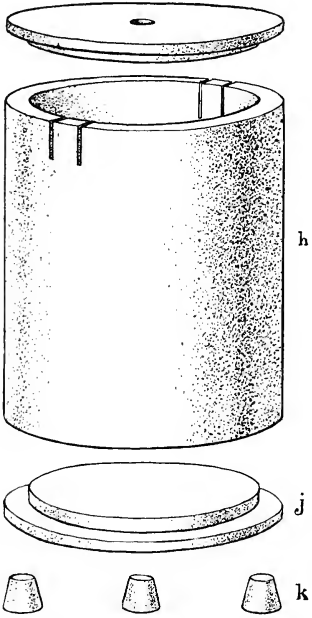

Fig. VII.

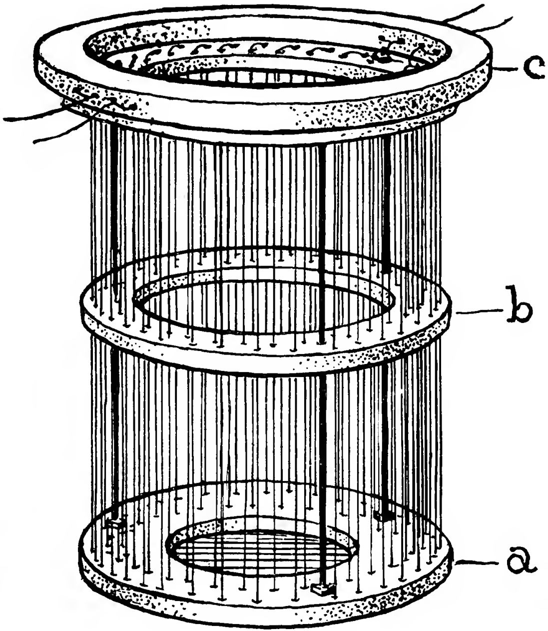

Fig. VI

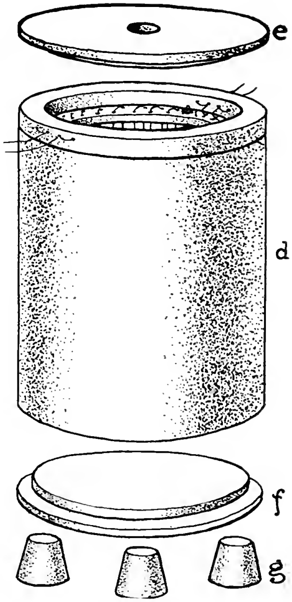

Fig. VIII.

planation of so many failures is very simple: *The cell wall must not be weakened at any point by the pressure of the cutting tools*; because, when the cell is baked, the shrinking material (the shrinkage is about 10 per cent.) necessarily draws away from places of relative weakness towards those where the cohesion of the particles is stronger, and *cracks* are developed. It is by no means necessary that the damage done by irregular pressure from the tools, or by too great pressure, should be obvious in the finished cell. In fact, it is rarely discovered until the cells are taken from the kiln. At first, our failures from the cause alluded to were over 90 per cent. At the present time, about 10 per cent. of the cells develop cracks while in the kiln. The improvement has been due, in a large measure, to improvements in the cutting tools and to the increased attention which has been given to keeping them in good condition. The usual lathe cutting tools were found to be ill-adapted to the work, and it was necessary to design others with new forms of cutting edge. But, however good in general the design of the tool may be, failure is bound to attend its use in this work unless the cutting edge conforms at all times to the principles which good mechanics *feel* and practice by, even when they do not understand them.

The cylinder of compact clay, as it comes from the press, is shown in Fig. IV. It is placed in a chuck of special design, and cut by tools, likewise of special design—and at a speed which the operator has found to be best adapted to his purpose—into the form shown in Fig. V. The many details of the operation are omitted because it is not believed that their publication in the fullest manner would lead to the manufacture of the much-needed supply of good osmotic cells, and because, to most of our readers, they would be unnecessary and irksome.

D. The Burning and Glazing of the Cells.

Nearly all of our experimental work in the baking of clays was for several years done in an electric kiln which was designed for the purpose. A description of it has been published elsewhere,[1] but we venture to reproduce the cuts of it

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[1] THIS JOURNAL, **32**, 93.

here, in the first full account of the method of making cells, because of the important part it has played in the successful solution of that difficult problem. It is shown in Figs. VI, VII, VIII and IX. It will be seen to consist (Fig. VI) of platinum wires, threaded through three clay rings, which are held apart by three platinum rods. The rods expand in the same degree as the wires, and thus keep the latter always taut, whatever may be the temperature of the furnace. The wires are in two pieces of equal length, so that they may be placed in series or parallel, according to the amount of current which it is desired to use. Fig. VII shows the furnace in place in the innermost of the clay cylinders which surround it when in use. The other clay cylinder, the outer one, is shown in Fig. VIII. Fig. IX exhibits all the parts of the kiln in their mutual relations, though, as will be seen by the figures, the original drawing was made to illustrate the use of the instrument as a crucible furnace. The kilns (of which we had three in use) were all calibrated by means of a Le Chatelier pyrometer. They thus became, in themselves, *resistance pyrometers*, the temperature of which could be easily ascertained at all times. A Seger gas experimental kiln was also used at different times, especially when we were trying to develop a suitable glaze for the cells.

The electric kiln answered well every purpose for which it was constructed up to about 1200°, *i. e.*, to a temperature at which platinum begins to volatilize in an atmosphere containing oxygen. At higher temperatures, the loss of platinum from this cause was sufficient to make necessary a frequent recalibration of the kilns. Fortunately, when we were in trouble in consequence of this phenomenon, we were offered the free use of the kilns of the Chesapeake Pottery Co. by the late president of that concern, Mr. D. F. Haynes. At the pottery we could neither control nor know with certainty the temperature of any part of the kilns, but it was easy to find the places in them where the best results were most frequently obtained. Since then, all of the cells have been burned at the pottery.[1] In general, the hotter parts of the kilns, where

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[1] It should be stated also that we are under great obligation to the superintendent of the Chesapeake Pottery, Mr. Thomas Mayer, for his friendly coöperation.

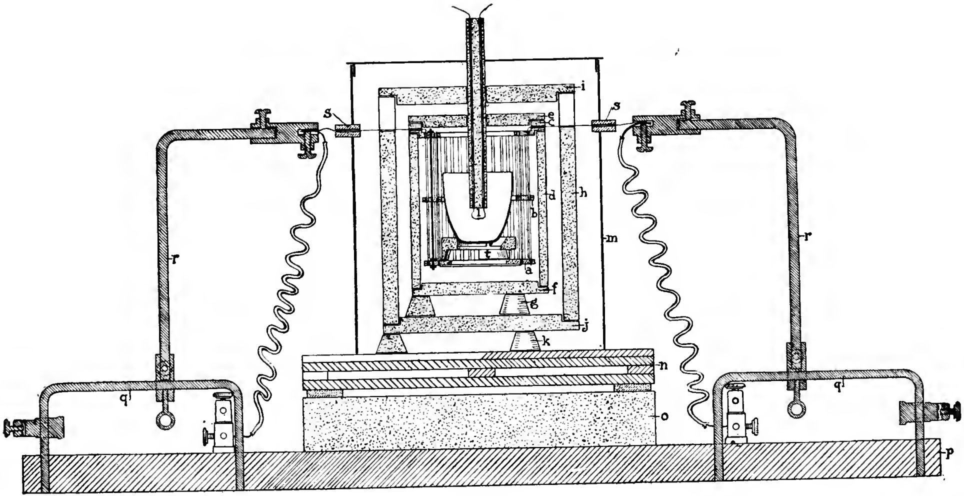

Fig. IX.

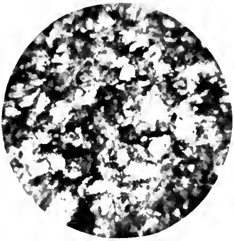
Fig. X.

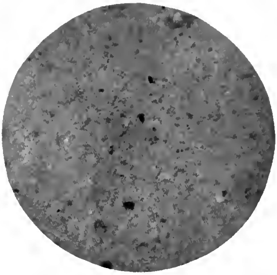
Fig. XI.

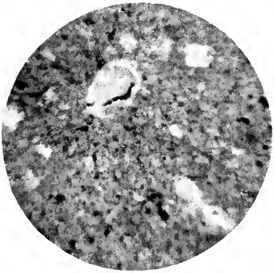
Fig. XII.

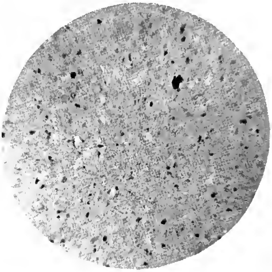
Fig. XIII.

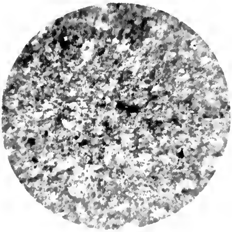
Fig. XIV.

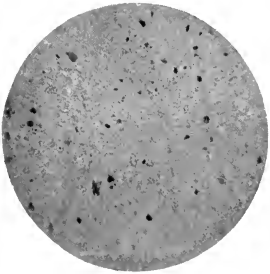
Fig. XV.

the temperature is certainly above 1200°, but probably somewhat under 1400°, are selected.

It has been stated elsewhere that in our endeavor to produce the correct texture of cell wall, we made a study of thin sections, both of the potters' cells and of our own products. In the course of this work a considerable number of photographs have been accumulated, six of which are here reproduced. Three of them (Figs. X, XII and XIV) are from potters' cells, and three (Figs. XI, XIII and XV) are from the first cells made by us which proved themselves well suited to the measurement of osmotic pressure. It will be noted that the texture of the cells made in the laboratory is incomparably finer (closer) than that of the potters' products. But we are convinced, after five years of laborious investigation, that just this *excessive fineness of texture* is absolutely *indispensable* to the correct measurement of osmotic pressure. It is necessary, in the first place, in order that the membrane may be deposited *exclusively upon the inner surface* of the cell wall; and it is necessary, also, in order to give the membrane a *backing* which will enable it to withstand pressure. If the texture is more open than that shown in Figs. XI, XIII and XV, the membrane is deposited, at least partially, *within* the wall, and it breaks under moderate pressure.

An explanation is called for of the numerous black specks which are seen upon Figs. XI, XIII and XV. They are particles of the emery which was used in grinding the sections, and no part of what the photographs are intended to show. Unfortunately for the progress of the work, we have been obliged to make excursions into many fields previously unfamiliar to us, and one of these was that of *microphotography.* This will accouut for any defects which an expert may detect, including a failure properly to cleanse the sections before photographing.

We are unable to state at the present time the exact extent to which the sections here reproduced were magnified, the orginal records having been mislaid or lost, but it is believed to have been 125 diameters.

The question naturally arises, whether it is possible to make the texture of a cell wall *too close.* We cannot answer the question positively, but we are inclined to think that it is; for, in some cases where the cells had been baked at very high temperatures, and had, in consequence, suffered an unusual amount of contraction, it was found that the membranes would not adhere well to the walls. A tentative explanation is that the membrane, though deposited in general on the surface, must be *rooted* somewhat into the wall (the pores) in order to adhere to it firmly. This assumption appears to be in accordance with the little evidence which has been gathered through microscopic examination.

After baking the cells, and before glazing them, they are ground under the shoulder to fit the brass rings with which the manometers are fastened in place. The necks also are ground to the exact taper of the brass cones upon the ends of the manometers, a high speed carborundum wheel being employed for the purpose.

The finding of a suitable glaze for the upper half of the cells was a matter of considerable difficulty. As might have been expected, the expansion coefficient of products made as these cells are is very different from that of any of the potters' wares, hence none of the glazes which are used by the potters would meet our requirements. All such glazes were found to "craze" badly upon the biscuit. An attempt was made to glaze with feldspar, but with poor success. A wholly suitable glazing material was finally obtained by adding silica and feldspar to one of the glazes which is used by the potters on the better grades of their white table ware. The earlier experiments in glazing were carried out at the laboratory in a Seger gas kiln, but at the present time the cells are glazed at the Chesapeake Pottery.

There is one objection to glazing the cells, to which attention should be called. They are glazed, inside and outside, from the middle upwards. The whole of the interior surface of the cell is covered either by the glaze or by the membrane, so that no material in solution can diffuse into the cell wall from the inside. On the outside, the case is different; there it is quite possible for dissolved substances to diffuse

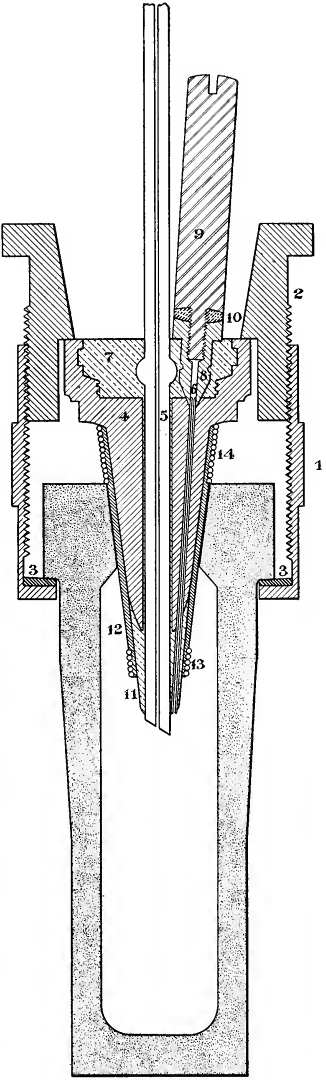

Fig. XVI.

in and to accumulate between the inner and the outer glazed surfaces. If these should afterwards diffuse downward and distribute themselves about the membrane, the pressure measured would evidently not be that of the solution within the cell, but the difference between the pressures of the two solutions on the opposite sides of the membrane. This possible vitiation of the results has been a source of much anxiety, and we have endeavored to guard against it by soaking the cells continuously, when not in actual use, in pure water which is frequently renewed. A radical remedy for the difficulty would be a cell, the upper half of which is entirely nonporous; and we have been endeavoring for the past three years to produce a cell, the upper half of which would become porcelain on baking, while the lower half remained porous and suitable for the deposition of a membrane. The results have not been wholly satisfactory up to the present time, but we do not yet despair of final success. The difficulty is, of course, that of producing clay mixtures for the two parts of the cell which shall maintain *identical expansion coefficients* throughout the whole of the baking and cooling periods; since otherwise cracks, or at least a condition of weakness, must develop at the junction of the two parts. This is believed to be the last of the many serious problems with which we have had to deal in the manufacture of osmotic cells.

E. The Manometer Attachments.

In 1908 we published a description[1] of the cell, with its manometer attachments, which was at that time in use. The improvements which have been made since then affect only the minor features, and none of them are of a radical character. They have nevertheless contributed materially to the ease and the accuracy of the measurements of pressure. Fig. XVI is intended to show every essential detail of the closed cell as it has been used throughout the recent work on the temperature coefficient of osmotic pressure. The function of the brass collar (1) and of the brass nut (2) will be readily understood without explanation. The form of these pieces

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[1] THIS JOURNAL, **40**, 266.

has varied but little during the past eight years. The lead ring (3) separates the shoulder of the cell from the flange of the brass collar and serves to protect the glaze upon the former. A ring of softer material than lead, *e. g.*, leather, cannot be used for the purpose, since any upward movement of the collar—due to diminishing thickness of the ring—would lead to an increase in the capacity of the cell and a dilution of the solution. In other words, the ring (3) must be of fairly rigid material. The brass cone (4) has two holes passing entirely through it, one for the manometer tube (5) and the other for the hollow needle (6), both of which (the manometer and the needle) are securely fastened in the cone by means of the Wood's metal (7). The holes through the cone are bored slightly larger than the tubes which are to occupy them, in order that the molten metal may flow down and completely fill the space between the latter and the walls of the former. In this way the tubes are fixed more firmly in their places, and all danger of leakage upwards through the cone is avoided. The hollow tube (6)—the needle—is nickel-plated and is brazed into the brass piece (8), which is bored out larger and threaded internally at the upper end to fit the closing plug (9). The upper end of (8) and the lower end of the larger portion of (9) are made concave in form, and between them is placed the grease-filled leather packing (10). The concave form of these two surfaces is essential, since it effectually prevents any outward lateral movement on the part of the packing and gives a tight joint under the highest pressures. After fixing the needle and the manometer tube (or rather, the tube which is to be fused to the manometer) in their places by means of the fusible metal, the cone (4) is extended by the Wood's metal seen at (11). The extension is for the purpose of covering and protecting the lower portion of the needle tube. Over the cone, thus lengthened by the Wood's metal, is slipped the rubber tube (12) which is tightly wound, at the lower and upper ends, with twisted shoemakers' thread (13, 14). Owing to the ease with which rubber always moves towards a region of smaller pressure, the whole space (14) between the shoulder of the brass cone and the top of the cell must be covered and rigidly supported by the thread. In practice, the winding of the upper end of the rubber tube is carried so far down that the last two or three turns of the thread are actually within the neck of the cell when it is closed for a measurement of pressure.

A manometer, on whose calibration and verification weeks, and perhaps months, of labor have been bestowed, is too precious an instrument to be unnecessarily exposed to danger. Hence the cones are not attached in the first instance to the manometers, but always to short pieces of tubing of the same kind, which are afterwards fused to the manometers or cut off from them, as occasion may arise.

The finished cell, as described above, is satisfactory in all respects, except in the one particular already alluded to, namely, that there is a *chance* that dissolved matter may diffuse in between the two glazed surfaces and afterwards affect the measurement of pressure in the manner which has been explained. It is not believed, however, that any of our results have been vitiated in the slightest degree from such a source. Nevertheless, it would give us great satisfaction to remove the danger altogether by making a cell half porous and half porcelain, which would not require glazing; and it is in this direction only that any further improvement of the cell is anticipated.

JOHNS HOPKINS UNIVERSITY,
Dec. 1, 1910.

THE ABSORPTION SPECTRA OF CERTAIN SALTS OF COBALT, ERBIUM, NEODYMIUM AND URANIUM AS AFFECTED BY TEMPERATURE AND BY CHEMICAL REAGENTS.[1]

BY HARRY C. JONES AND W. W. STRONG.

PART II.

Introduction.

In the absorption spectra of salts in solution, very few of the salts having characteristic banded spectra show much,

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[1] The first part of this article was published in THIS JOURNAL, **45**, 1.

if any, influence of the acid radical. In the case of uranium salts there are, however, several exceptions. One of these is the aqueous solution of the nitrate and the other salts. The nitrate bands have been shown to have shorter wave lengths than those of the other salts. In the following description a detailed account will be given of the changes of the spectra as the nitrate is gradually changed into the sulphate or the chloride.

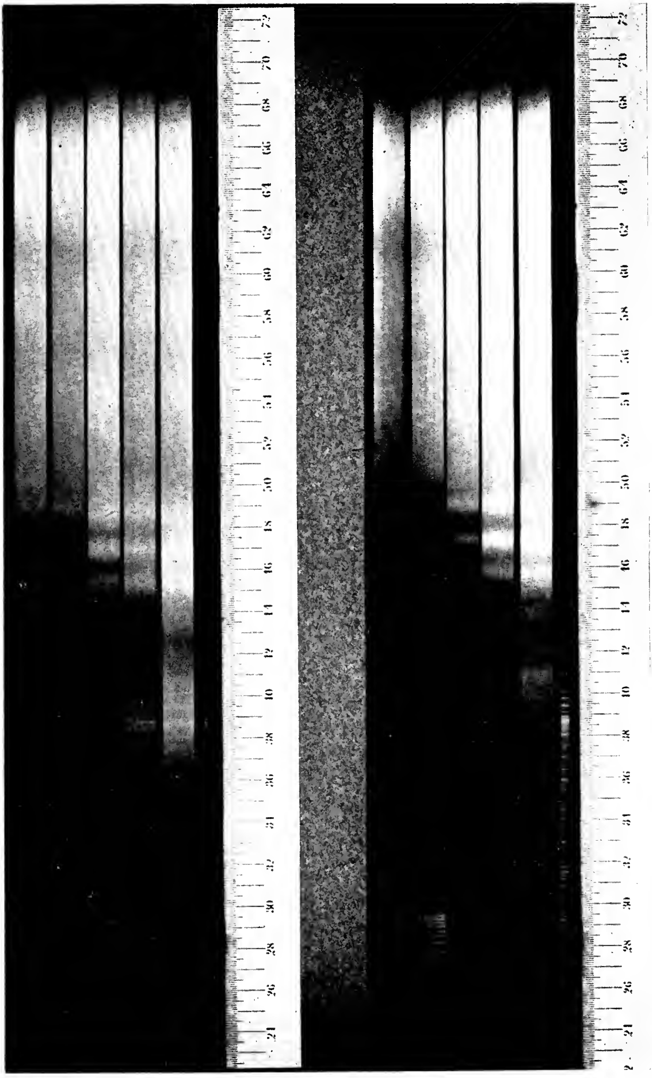
Spectrophotography of Chemical Reactions of Uranyl Salts.

In Plate VIII is shown the absorption spectrum of an 0.08 normal solution of a uranyl salt in water 15 mm. in depth. Beginning with an 0.08 normal solution of uranyl nitrate, sulphuric acid was added so as to make the concentration of acid, beginning with strip 1, as follows: 0.37, 0.73, 1.46, 2.92, 5.84, 10.22, and 14.60 normal.

In strip 1 there is practically the sulphate spectrum, most of the nitrate having been transformed. The addition of more acid does not produce any marked change until we reach the sixth and seventh strips. The *c* and *d* bands are very

	Nitrate bands.	Sulphate bands.	Strip 1.	Strip 5.	Strip 6.	Strip 7.
				5230?		
				5200?		
				5170?		
				5100?		
				5000?		
a	4890 4800	4900	4900 to 5100	4910	4920	4920
b	4742 4722	4740	4730	4750	4740	
c	4540	4580	4570	4570	4570	4550
d	4390	4460	4440	4450	4480	
e	....	4330	4320	4340	4340	4370
f	4155	4200	4200	4200	4210	4225
g	4030	4070	4070	4070	4080	4090
h	3905	3970	3950	3970	3960	3970
i	3815	3850	3850	3850	3860	3860
j	3710	3740	3720	3740	3750	3760
k	....	....	3620	3620	3640	3650
l	3515	3530	3520	3520	....	....

Plate VIII.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A
B

greatly shifted, so that in the latter strip they form a single band. Several of the other bands are considerably shifted towards the red. Throughout the changes of conditions above named, the bands remain quite sharp and well defined (for uranyl bands), and change very little in intensity. This is in quite marked contrast with many of the plates in which there are certain stages that hardly show any uranyl bands at all, whereas at other stages the bands are very strong indeed.

The bands in the upper strips beyond the region λ 5000 are probably due to nitric oxide. Several of the bands are quite strong.

The simplest interpretation of this plate is that as more and more sulphuric acid is added molecules are formed that contain more and more of the acid. That there are several of these compounds formed seems probable, since the shift of the bands is quite large and this shift takes place gradually.

	Nitrate bands.	Chloride bands.	Strip 1.	Strip 6.	Strip 7.
a	4890 4800	4920			
b	4742 4722	4740	4700 weak and broad	4720	4740
c	4540	4560	4560 weak and broad	4580	4580
d	4390	4460	4410 weak and broad	4430	4440
e	....	4315	4270 strong	4280	
f	4155	4170	4140 strong	4145	
g	4030	4025	4020 strong	4020	
h	3905	....	3900	3900	3900
i	3815	....	3800	3800	
j	3710	....	3700	3700	3700 weak
k	....	....	3600	3600	3600 weak
l	3515	....	3500	3500	

Plate XIII, *A*, shows the effect of adding sulphuric acid to an aqueous solution of uranyl nitrate. The first strip here gives the absorption of uranyl nitrate to which no acid has been added. The changes here are from the neutral nitrate bands to the neutral sulphate bands, approximately. There is in this case a gradual shift of the bands to the red.

The effect of adding hydrochloric acid to an aqueous solution of uranyl nitrate was studied. The depth of cell was

15 mm. The concentration of the uranyl salt was kept constant. The percentages of acid were increased.

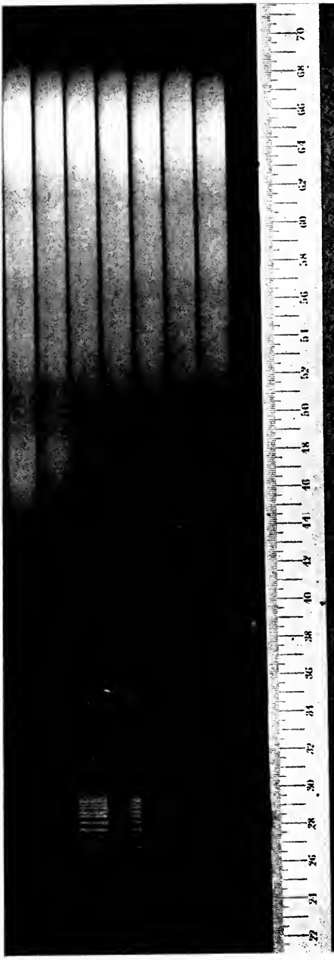
In the first strips of the spectrograph the *b* and *c* bands are very weak. They become stronger and shift gradually to the red. The other bands are quite sharp until the last strip, where they appear very weak. Their wave lengths are but slightly changed. In the above table the wave lengths of the neutral chloride and nitrate bands are taken from the other tables.

Plate XIII, *B*, represents the absorption spectra of uranyl nitrate to which acetic acid had been added. Plate XII, *A*, represents the same effect, except that here the original uranyl nitrate solution was only 1 mm. in thickness, so that the ratio of acetic acid to the amount of uranyl salt was much larger.

	Uranyl nitrate.	Strip 1. Plate XIII, B.	Strip 6. Plate XIII, B.	Strip 1. Plate XII, A.	Strip 3. Plate XII, A.	Strip 5. Plate XII, A.	Uranyl acetate.
a	4890 4800	4830?					
b	4742 4722	4660	4675			4860	4900
c	4540	4510	4520		4650	4720	4770
d	4390	4370	4380	4420 weak	4500	4570	4600
e	....	4245	4250	4270	4350	4440	4460
f	4155	4130	4140	4150	4220	4340 4220	4320 4200
g	4030	4020	4030	4020	4030	4120	4090
h	3905	3910	3920	3910	3910	4010	3975
i	3815	3800	3810	3800		3870	
j	3710	3670	3700	3700		3770	
k	....	3570	3580	3600		3670	
l	3515	3460	3460				

The first effect which the addition of acetic acid produces is to shift slightly the uranyl bands of the nitrate to the red, and to cause them to become much sharper. When some twenty times as much strong glacial acetic acid had been added as was equivalent to the uranyl nitrate solution, the uranyl bands became quite weak, and shifted very greatly towards the red, as is shown in Plate XII, *A*. The *e* and *f* bands are each shifted nearly 200 Angström units. When

Plate IX.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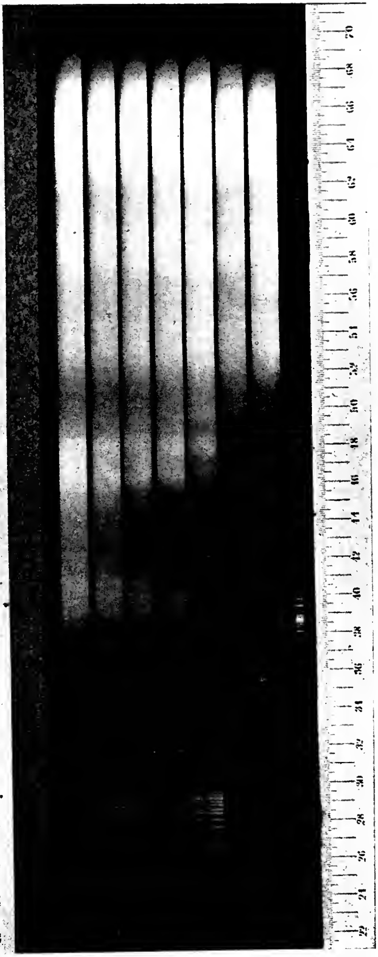
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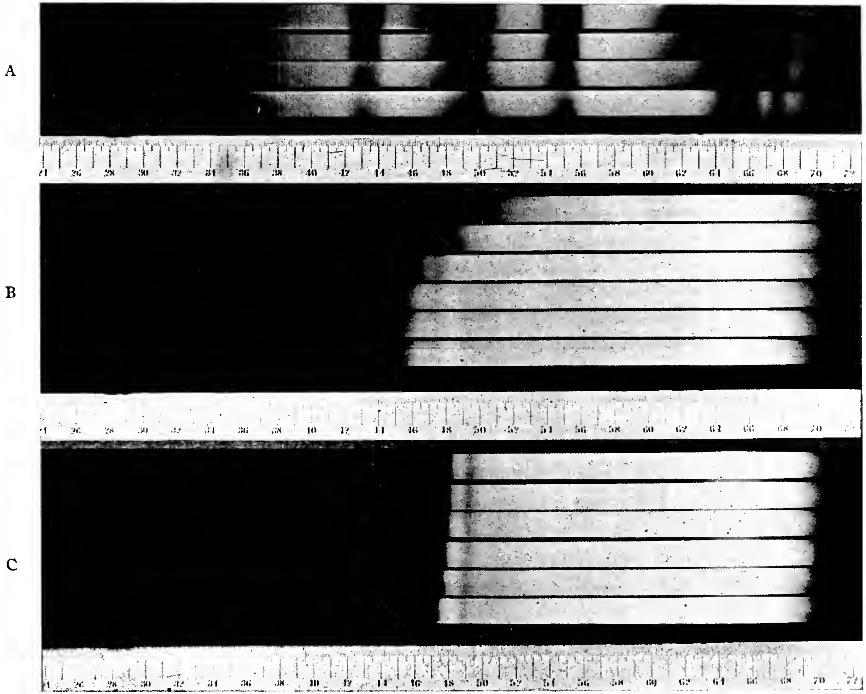
Plate X.


A
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B
24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72
C
24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72

this enormous shift towards the red takes place a *new* band appears between *f* and *g*. This new band will be called f_1. Further addition of acetic acid causes the uranyl bands to become stronger again, producing at the same time a small shift to the red.

Uranyl Chloride in Glycerol.

Plate IX, *A* and *B*, represents the absorption spectra of a solution of uranyl chloride in glycerol, the depths of cell being 10 and 5 mm., respectively. The concentrations, starting with the strip nearest the scale, were 0.176, 0.132, 0.088, 0.059, 0.041, 0.032, and 0.022 normal. The spectrograms are very similar to those of the other uranyl salts. The blue-violet absorption band vanishes at about λ 4300. The positions of the uranyl bands are: *a*, 5050; *c*, 4720; *d*, 4540; *e*, 4400; *f*, 4260; *g*, 4140; *h*, 4025; and *i*, 3920.

The uranyl bands of a glycerol solution are quite broad. The same is true of the uranous bands. Glycerol usually has the effect of making the bands less dense than they appear for most of the other solvents. In a few cases the bands are quite fine, however, as in the case of the erbium and neodymium salts.

Uranous Salts.

Uranium was discovered in 1789 by Klaproth and was named to commemorate the discovery of the planet Uranus by Herschel in 1781. Quite a large number of oxides are known.

The orange oxide, $UO_3(UO_2O)$, or uranyl oxide, is obtained by heating uranyl nitrate slowly as long as acid fumes escape. When the nitrate is rapidly decomposed a red modification of the oxide is produced. All the uranyl salts may be considered as compounds of UO_3 where one of the oxygen atoms has been replaced by an acid or halogen radical. Aqueous solutions of the uranyl salts are partly hydrolyzed. The nonhydrolyzed portion dissociates in the usual way.

Urano-uranic oxide, U_3O_8, is obtained by heating uranyl nitrate to a high temperature.

The oxide UO_2 is obtained by heating the oxide U_3O_8 in a current of hydrogen, and is of a brown or copper-red color. The reduction of an oxide of uranium to the oxide UO_2 and weighing is an analytical method of estimating uranium. This oxide in acid solutions forms the green uranous salts.

The oxide U_2O_5 is formed when ammonium uranate is strongly ignited in air. The oxide UO_4 is formed when a dilute solution of hydrogen peroxide is added to uranyl nitrate. The uranates have the general formula $R_2U_2O_7$, as, for example, potassium uranate, $K_2U_2O_7$. When alcohol is added to a solution of hydrogen peroxide, uranyl nitrate, and sodium hydroxide (a minimum amount of the hydroxide), golden yellow needles crystallize out having the composition $(NaO_2)_2UO_4.8H_2O$.

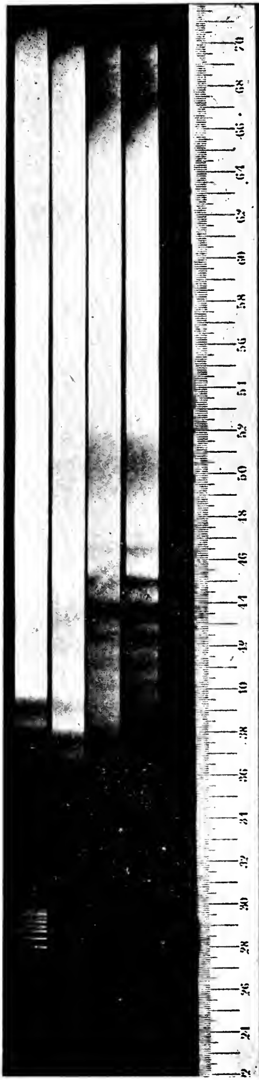
Very little work has been done up to the present on the absorption spectra of uranous salts, largely because of their very unstable character in solution. J. Formánek describes the absorption spectra of uranous chloride. This was prepared by adding a little zinc and hydrochloric acid to a uranyl chloride solution. He found that the spectrum changed as the uranyl chloride was being reduced. A very strong band was found at λ 6507. The other bands, eleven in number, were $\lambda\lambda$ 6722, 6367, 6165, 6030, 5782, 5497, 5238, 5064, 4962, 4840, and 4519.

A similar method has been used by the authors. The uranous nitrate, sulphate, and chloride were formed by adding the corresponding acid to a solution of the uranyl salt containing some zinc. The uranous chloride and sulphate were quite stable in solution, remaining reduced for weeks. Uranous sulphate crystallizes out from solution as $U(SO_4)_2.9H_2O$. Solutions in alcohol can be reduced just as easily as solutions in water. Uranous nitrate was found to be very unstable. At the present writing a number of spectrograms have been made, and much more work will be done on these uranous salts and on the absorption spectra of the various oxides. It has already been found that uranous chloride has very different spectra in different solvents.

Uranous Chloride in Water.

A solution of uranous chloride in water was made in the

Plate XI.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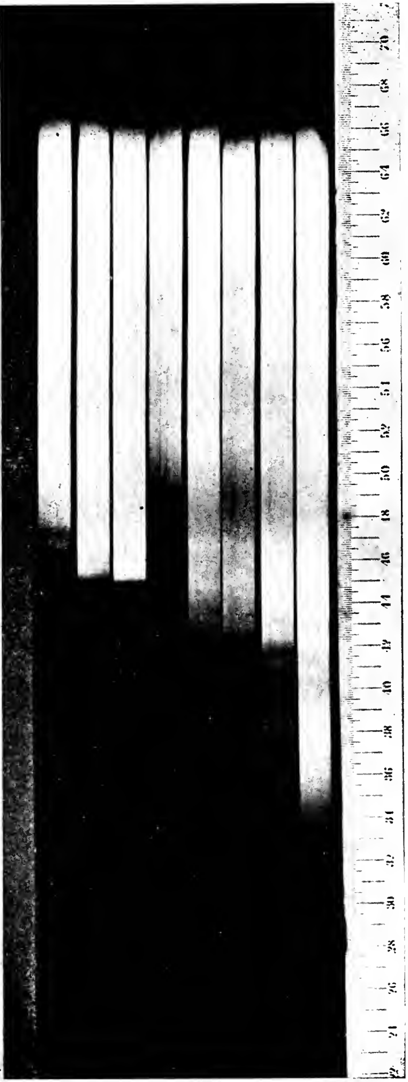
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Plate XII.

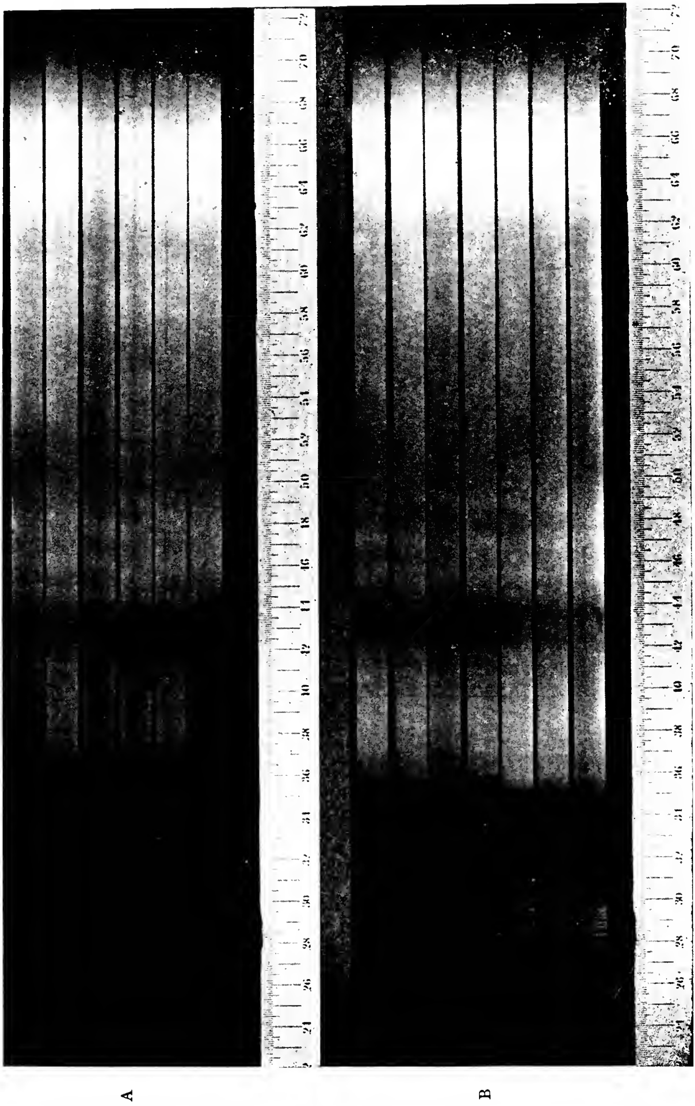
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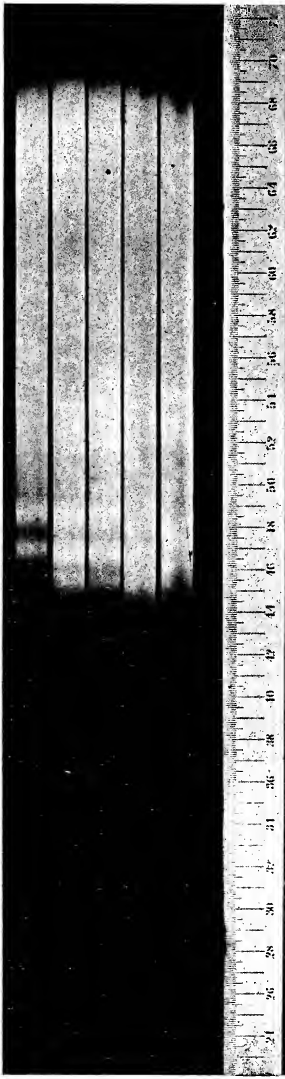
Plate XIII.



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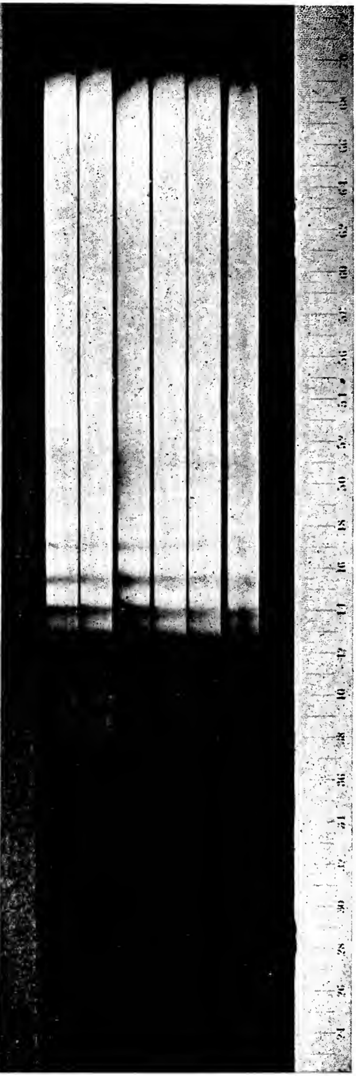


B

usual way. This solution was of a dark green color even when very dilute. When sufficiently dilute most of the uranous salt came down as a precipitate after standing for several days. The solution was examined spectroscopically, it being practically colorless to the naked eye. The absorption spectrum corresponded closely to that of the uranyl chloride bands of water. The bands *e*, *f*, and *g* appear with considerable intensity, while the other bands are very weak, *e* consisting of two bands of about equal intensity and very close together. The wave lengths of the bands are approximately as follows: λ 5030 (weak); *a*, λ 4910; *b* (very weak), λ 4790; *c* (very weak), λ 4550; *d* (very weak), λ 4420; *e*, λλ 4305, 4270; *f*, λ 4150; and *g*, λ 4020.

The spectrogram (Plate XIV, *A*) represents the absorption of a 0.17 normal solution of uranous chloride in water. Starting with the first strip the depths of cell are 1.2, 2, 4, 8, 16 and 32 mm. For the first three strips the exposures were for 3 minutes to the Nernst glower for all the spectrum, 3 minutes to the ultraviolet, and 1 minute to the spark. The other three strips were exposed to the Nernst glower for 3 minutes. The slit width was 0.15 mm. and the current in the glower 0.9 ampere. No exposure to the ultraviolet was made for the upper strips, as it was considered that this region would be entirely absorbed. The spectrogram shows, however, that this would not have been the case.

Strip 1 shows complete ultraviolet absorption up to about λ 3300. Two absorption bands, λλ 4200, 4400, almost merge into each other. Of these the one with shorter wave length (λ 4270) is considerably stronger than the other (λ 4370). A strong band appears at λ 4980, about 30 Angström units wide. This is limited by a wide region of general absorption, which widens out very rapidly towards the violet with increasing depth of cell. This is most likely due to the presence of diffuse bands in this region. The diffuse band at λ 5500 widens symmetrically with increasing depth of cell. There are two very strong bands which for 2 mm. depth of cell are situated at λ 6430 to λ 6620 and λ 6720 to λ 6770. This region of absorption is a very characteristic one for uranous chloride in water. Other diffuse bands appear at λ 3910, λ 4030, λ 4600, and λ 6340.

Uranous and Aluminium Chlorides in Water.

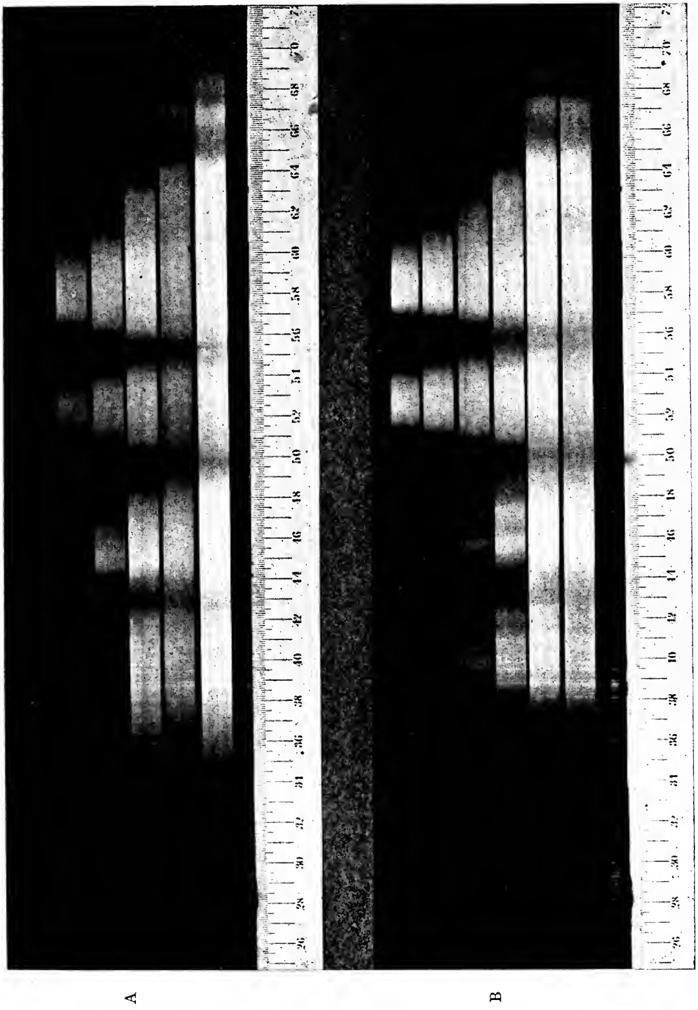
Uranyl chloride was reduced in the presence of an aluminium chloride solution of about 2.4 normal concentration. The concentration of uranous chloride was 0.17 normal. Plate XIV, *B*, represents the absorption spectrum, the depths of cell being 1.2, 2, 4, 8, 16 and 32 mm.

The resulting spectrum is very much like that of the pure aqueous solution. The ultraviolet absorption is much greater, the absorption extending to about λ 3800. The presence of aluminium brings out several bands in the blue-violet region which we shall continue to designate as the uranyl bands. These bands have the same wave lengths as the corresponding uranyl bands of a solution of uranyl and aluminium chlorides in water.

The band at λ 5000 is much more diffuse than the corresponding band for water. The band at λ 5570 widens symmetrically with increasing depth of cell. Besides these bands there are two bands at λ 6550 to λ 6640 and λ 6750 to λ 6800. The general effect of the aluminium chloride is to bring out the uranyl bands; to increase the ultraviolet absorption; to make the band λ 5000 and others slightly more diffuse and to cause the uranous bands to shift towards the red, about 20 or 30 Angström units.

The concentration of uranium in a solution necessary to bring out the uranyl bands either in the uranyl or uranous condition is about the same.

The spectrogram, Plate XXIV, *A*, shows the effect of the presence of aluminium chloride and hydrochloric acid upon the uranous bands. Strip 1 represents the absorption of a 0.17 normal solution of uranous chloride in water 3 mm. deep; strip 2 the same, to which a 3.04 normal solution of aluminium chloride had been added, so as to make the depth of cell 4 mm.; strip 3, a depth of cell of 6 mm.; strip 4 represents the same as strip 1; strip 5 shows the absorption of the solution of strip 4, to which sufficient hydrochloric acid had been added to make a depth of cell of 16 mm. Both alumin-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ium chloride and hydrochloric acid cause the ultraviolet absorption to increase very much. Aluminium chloride has much the same effect as hydrochloric acid, although not so great. It does not change the water bands λ 6400 and λ 6655 as does hydrochloric acid. Strip 3 shows bands at the following positions: *g*, λ 4140; *f*, λ 4280 (strong); *e*, λ 4400 (*e* and *f* almost merge into each other); *d*, λ 4490; *c*, λ 4620; *b*, λ 4780, λ 4990, λ 5550, λ 6460 to λ 6660, λ 6780.

Two cc. of a normal aqueous solution of uranyl chloride were added to 8 cc. of a 3.04 normal aqueous solution of aluminium chloride and to this were added 2 cc. of hydrochloric acid and zinc, so that the uranyl salt was reduced to the uranous condition. To a 2 mm. depth of solution was added water so as to make the depth of cell 7 mm. The addition of water caused the *b*, *c*, *d*, and *e* bands to become very faint and to be shifted to the violet. The band at λ 4980, and especially the bands at λ 5500, λ 6500, and λ 6750 were very considerably shifted. The solution of 7 mm. thickness showed bands at λλ 4130, 4210 (narrow), 4285, 4420(?).

Uranous Chloride in Acetone.

Plate XVII, *A*, strip 1, represents the absorption of a 1.8 mm. solution of uranous chloride in acetone, the solution having been made about 2 weeks before using; strip 2 represents the absorption of the same solution to which 0.5 mm. hydrochloric acid had been added; strip 3 the same as 1 to which 1.2 mm. of hydrochloric acid had been added (in this case a small amount of a brown precipitate was formed causing the absorption to be greatly increased); strip 4 represents an ether solution (ether was added to the acetone solution of uranous chloride, a deep green precipitate was formed and the ether became yellow) probably of uranyl chloride; strip 5 represents the absorption of an acetone solution of uranous chloride, freshly prepared, 2 mm. in depth; strip 6, the same, 5 mm. in depth; and strip 7, 14 mm. in depth.

The freshly prepared uranous chloride solution (in acetone) shows the uranous bands very faintly. The addition of hydrochloric acid is seen to bring out the bands very well.

In addition to the bands already described, faint bands (strip 2) appear at λ 6090, λ 6340, λ 6365, and λ 6390. The ether bands occur as follows: *a*, λ 4930; *b*, λ 4760 (a faint component at λ 4800); *c*, λ 4600; *d*, λ 4440; *e*, λ 4290; *f*, λ 4155; *g*, λ 4030. The shifts of the ether bands relative to the bands of the solution of uranous chloride in hydrochloric acid are very noticeable when the spectrograms are made to overlap. With reference to these bands the ether bands *d*, *e*, *f*, and *g* are shifted to the red and the *a* and *b* bands to the violet.

Uranous Chloride in Hydrochloric Acid and Acetone.

A 0.2 normal solution of uranyl chloride in strong hydrochloric acid was reduced by using as little zinc as possible. A plate showing the absorption spectra of this solution to which acetone has been added was made. Strip 1 represents the absorption of 5 mm. of the hydrochloric acid solution; strip 2 the same, to which 1 mm. of acetone has been added; strip 3, 3.3 mm. acetone; and strip 4, 12 mm. of acetone. The solution was thoroughly mixed in each case.

	Strip 1.	Strip 4.		
a	4980 (100 A. U. wide)	4925(20)		
b	4800	4760(20)		
c	4620	4590(s)	4535(15)	
d	4410	4425(s)	4470(f 20)	4380(f 20)
e	4280	4290(s)	4340(w20)	4240(w20)
f	4140	4160(s)	4200(w20)	4115(w20)
g	4010	4040		

In strip 1,[1] *a* consists of a strong broad band. As acetone is added this breaks into two components, the component of longer wave length disappearing as more and more acetone is added. In strip 1 there is a very diffuse band near the *d* band on the long wave length side. In addition to the uranyl bands there is a broad band at λ 5550; one from λ 6450 to λ 6680; and one from λ 6720 to λ 6820. In strip 4 all the broad uranous bands have disappeared and there remain only fine bands from 10 to 20 Angström units wide. These were located at λλ 6780, 6740, 6690, 6625, 6600, 6555, 6490, 6470, 6040, 6000, 5960, 5910, 5220, 5210, and 5195.

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[1] For this and other plates not reproduced in this paper see Publication No. 130 of the Carnegie Institution of Washington, by the authors of this paper.

Plate XV.

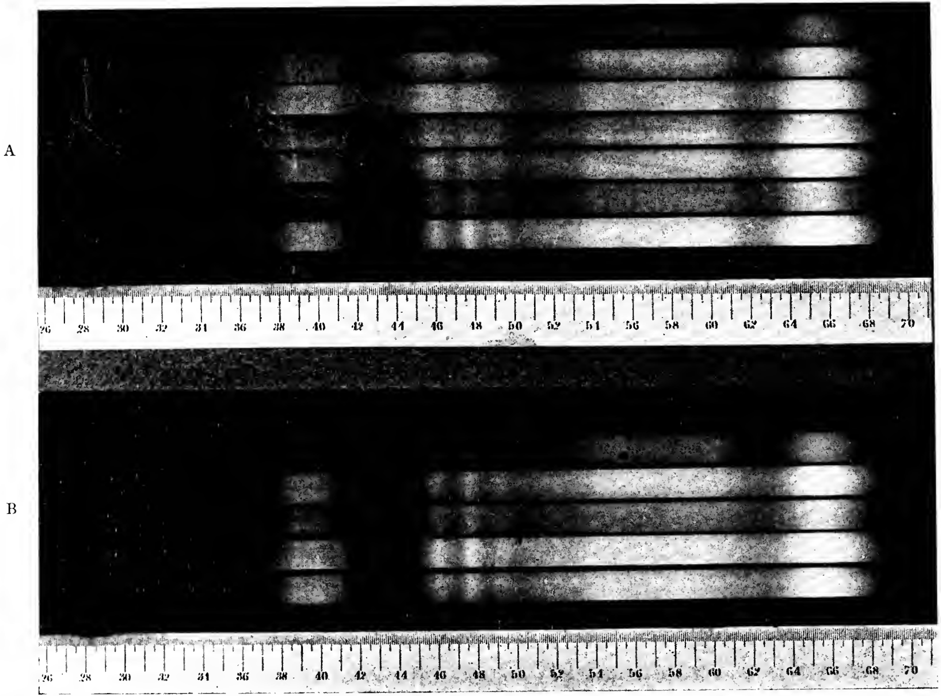
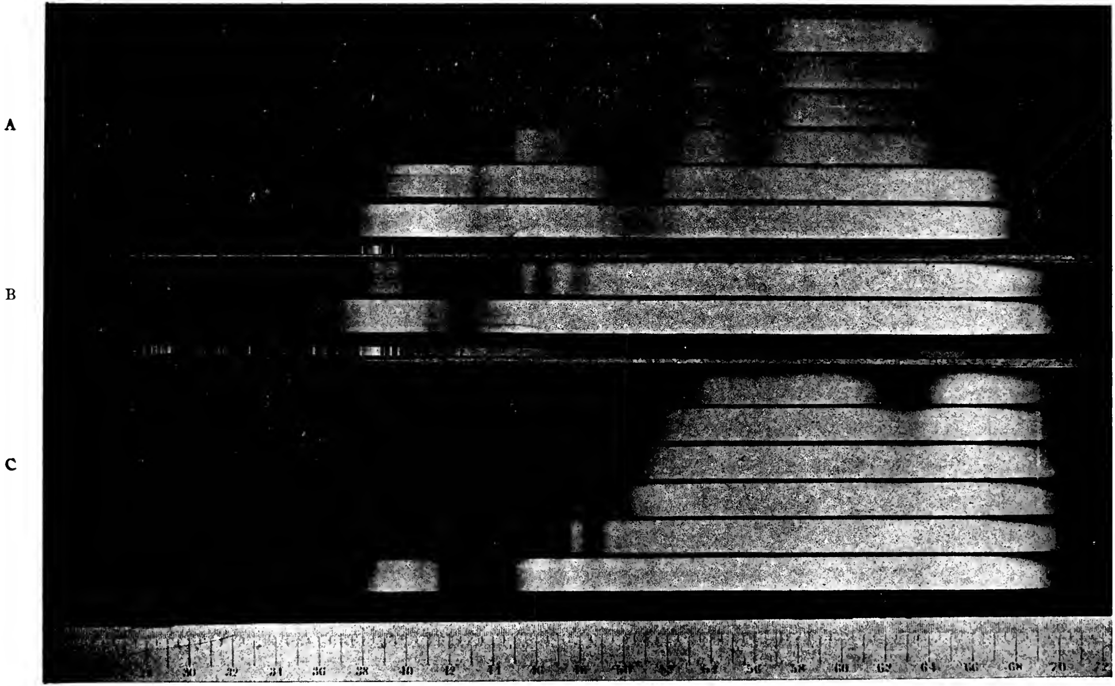

A
26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70
B
26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70

Plate XVI.



Uranous Chloride in Mixtures of Methyl Alcohol and Water and of Methyl Alcohol and Acetone.

A plate was made showing the absorption spectra of a constant amount of uranous chloride in mixtures of methyl alcohol and water (*A*), and of mixtures of methyl alcohol and acetone (*B*), the lower strip representing the methyl alcohol solution.

As the amount of water increases, the water band λ 6750 comes out gradually. The methyl alcohol band λ 5050 to λ 4850 is probably double. This narrows on the red side into a band at λ 4850. The methyl alcohol bands λ 4770 and λ 4600 practically disappear, and the band λ 4670 becomes very weak. In their places appear the water bands λ 4700 and λ 4550. The *de* band, λ 4300 to λ 4450, of the methyl alcohol solution weakens and breaks up, giving the *d* band at λ 4400 and the *e* band at λ 4280. This *e* band is a broadened band otherwise similar in appearance to the band λ 4300 in methyl alcohol, which appears quite narrow. The methyl alcohol bands *f*, λ 4230, and *g*, λ 4120, become the *g* water band at λ 4160, apparently by going together.

The most important change produced by adding acetone to a methyl alcohol solution of uranous chloride is to bring in a lot of narrow acetone bands in the region λ 6000 to λ 6500, and the strong absorption band from λ 6500 to λ 6800. There also appears a band at λ 5600.

Uranous Chloride in Water and Ethyl Alcohol.

The addition of ethyl alcohol (spectrogram XXIII, *A*) to an aqueous solution of uranous chloride causes a very marked change in the absorption spectrum, the water bands gradually disappearing and being replaced by ethyl alcohol bands. The spectrogram shows the decrease of intensity of the water bands very well. Strip 2 represents a 3.2 mm. depth of uranous chloride in water; 3 the same to which 1.2 mm. of ethyl alcohol has been added; 4, the same as 3, to which 2.2 mm. of ethyl alcohol has been added; 5 is the same as 4, plus 6 mm. ethyl alcohol; 6, the same as 5, plus 10 mm. ethyl alcohol. The upper strips are weak on account of the formation of a precipitate.

Uranous Chloride in Acetone and Water.

A plate was made showing the absorption spectra of uranous chloride in mixtures of acetone and water, *A* representing the more dilute solution of uranous chloride. The lower strip represents the absorption of an almost pure acetone solution, the other strips representing the absorption of the same solution to which greater and greater amounts of water are added.

This spectrogram shows that several of the uranyl bands are characteristic of acetone and aqueous solutions. The absorption of an acetone solution in the region λ 6500 is much less and consists of but a single band. The aqueous solution, on the other hand, has a very characteristic band at λ 6750. The band at λ 5550 of the acetone solution is shifted towards the violet as water is added.

As the percentage of acetone is decreased the acetone bands, *a*, λ 4920, *b*, λ 4750, and *c*, λ 4590 gradually disappear, while the water bands *a*, λ 4980, *b*, λ 4700, and *c*, λ 4570 gradually increase in intensity. No shift is to be noticed.

The other uranyl bands appear but slightly changed, the positions and intensities of the acetone and water bands being about the same. For the acetone solution they are *de*, λ 4430; *f*, λ 4290; g, λλ 4160, 4130; *h*, λλ 4040, 4010; and *i*, λ 3910. For the aqueous solution they are *de*, λ 4450 (weak), *f*, λ 4290; g, λ 4150; and *h*, λ 4010.

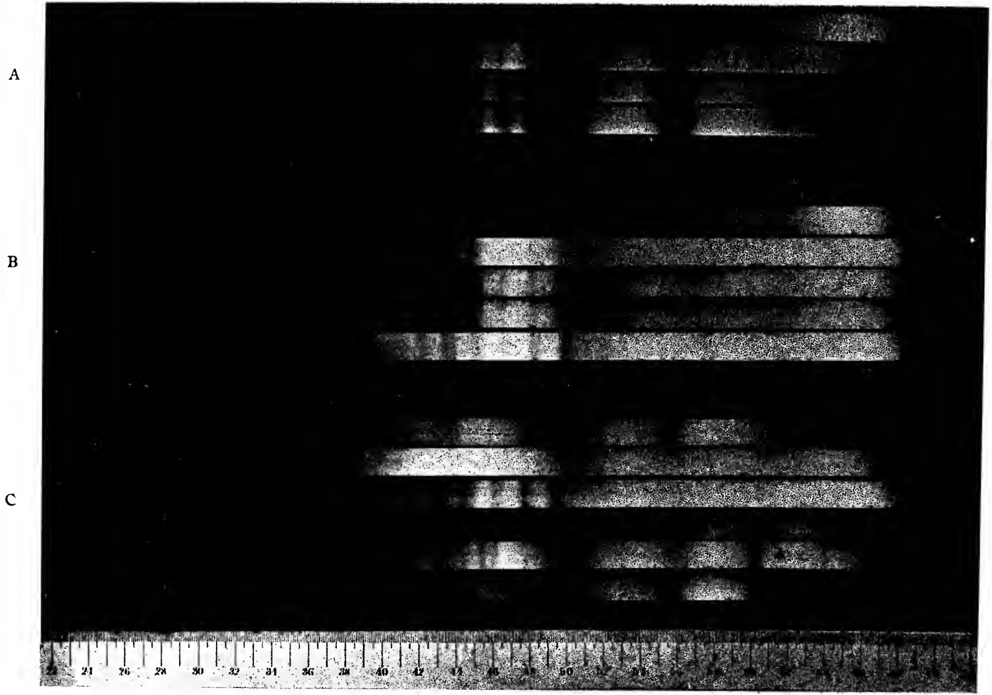
Uranous Chloride in Methyl and Ethyl Alcohols.

In the spectrogram, *A* represents the absorption of a dilute solution of uranous chloride in ethyl alcohol, and *B* in methyl alcohol. The depths of cell were 3, 6, 12, 24 and 35 mm., slit width 0.15 mm., exposure to Nernst glower 1.5 minutes to the whole spectrum, 2 minutes to the ultraviolet of the Nernst glower, and 1 minute to the spark.

The absorption of the two solvents is very much the same, the bands being much alike in intensity and position. The methyl alcohol bands are of slightly shorter wave lengths.

Ethyl alcohol solution: λ 4290 (narrow), λ 4710, λ 4950 to λ 5050, λ 5280 (weak), and λ 6200 to λ 6300.

Plate XVII.



Methyl alcohol solution: λ 4000, λ 4130, λ 4250, λ 4290 (narrow), λ 4700, λ 5020, λ 5260, and λ 6150 to λ 6300.

A solution of uranous chloride in methyl alcohol stood for almost a year. The absorption of this solution was quite different from that described above. This was probably due to the much larger amount of hydrochloric acid and zinc chloride in the old solution, as small amounts of hydrochloric acid as possible having been used in the solution described above. The positions of the bands of the "old" solution were: λ 3910 (double), λ 4020 (double), λ 4130 (double), λ 4590, λ 4750, λ 4710, λ 5000, λ 5550, and λ 6500 to λ 6800.

Uranous Chloride in Glycerol.

To make a glycerol solution of uranous chloride a strong solution of uranous chloride is made in some other solvent and is then mixed with glycerol and warmed. The warming is continued until as much as possible of the other solvent has evaporated. Spectrograms were then made with different depths of this solution, and of solutions in mixtures of glycerol with some other solvent. Plate XVI, *C*, represents the absorption spectra of a glycerol solution of uranous chloride of different depths; starting with the lowest strip the depths are 3, 4, 6, 9, 12, 18 and 24 mm. As the reduction was not complete it is impossible to know the concentration of the uranous chloride, although this could be found approximately. The spectrogram shows the uranyl bands and the uranyl blue-violet band. Knowing the depth of layer and having made the spectrogram it is possible to determine quite accurately the amount of uranyl chloride in the solution. The remainder of the uranium chloride is probably in the uranous condition.

The uranyl bands, *i*, λ 3800, *h*, λ 3930, and *g*, λ 4050, are very weak and about 60 Angström units broad. The band *f*, λ 4170, is fairly strong, as is also *e*, λ 4310; *d* is double, consisting of a wide diffuse band at λ 4440 and a narrower diffuse band at λ 4530; *c*, λ 4680, and *b*, λ 4840, are both very strong, and about 80 Angström units wide; *a*, λ 4980, is very narrow and has a very weak band at about λ 5060. The weak band at λ 5060 is barely visible in the original negative. For the greater depths of cell, bands several hundred Angström units wide and extremely diffuse appear at about λ 5300, λ 5600, and λ 6300. These will be more fully discussed when uranous chloride in mixtures of glycerol and other solvents is discussed.

Uranous Chloride in Mixtures of Glycerol and Water.

The spectrogram, Plate XV, *A*, represents the absorption of a solution of uranous chloride in glycerol to which water is added. Strip 1 represents the absorption of a 6 mm. solution of uranous chloride in glycerol; the other strip shows the effect of adding water, the amount of water added being very small for the first few strips.

For strip 1 the absorption consists largely of the bands *a*, λ 5000 (very broad and probably double); *b*, λ 4840; *c*, λ 4680; *d*, λ 4530, λ 4440 (latter component very strong); *e*, λ 4310; *f*, λ 4170; and *g*, λ 4050.

The addition of water causes the absorption in the region λ 6250 to increase. There are also broad absorption bands at λ 5000 and λ 5250, which are very diffuse and are somewhat stronger for the aqueous solution. The *b* glycerol band disappears entirely. The *c* glycerol band breaks up into two, and as the amount of water increases one of these moves rapidly towards the violet. The stronger component remains practically stationary. In strip 7 their wave lengths are λ 4565 (weak) and 4690 (strong and about 30 Angström units wide). The faint component of *d* disappears and there is left a very diffuse band at about λ 4420. The *e* band is double with components at λ 4250 and λ 4290. About these components there is a very considerable amount of general absorption. The *f* band is at λ 4150.

Uranous Chloride in Mixtures of Glycerol and Methyl Alcohol, Glycerol and Ethyl Alcohol, and Glycerol and Acetone.

The addition of methyl and ethyl alcohols causes very little change in the bands. Any large addition of acetone causes a precipitate to be formed.

Plate XVIII.

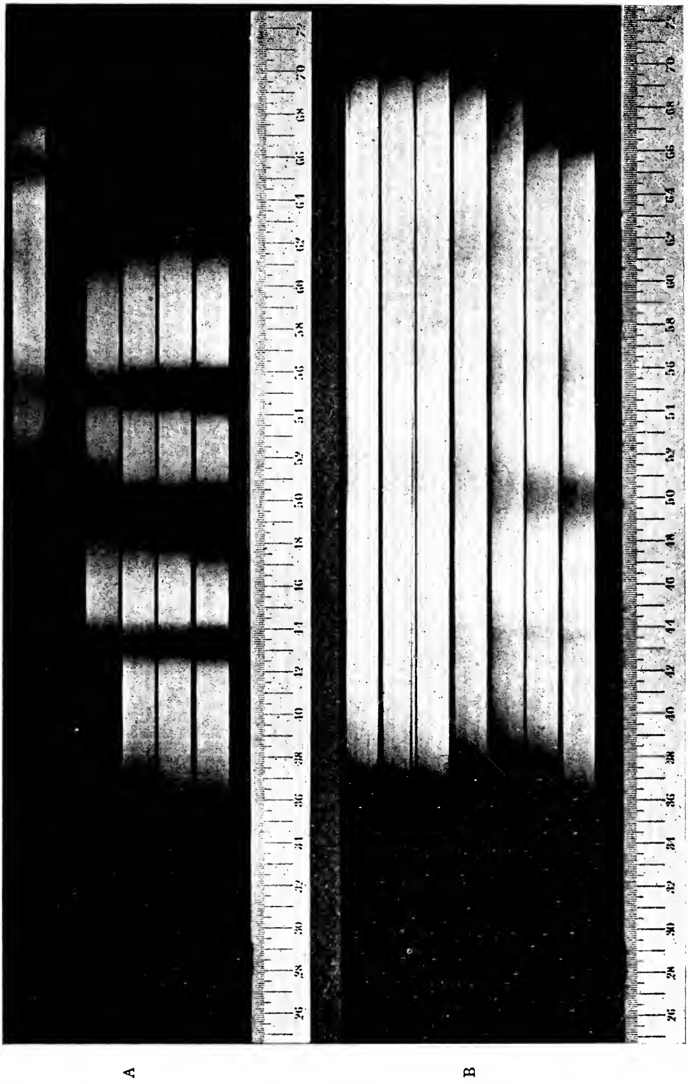

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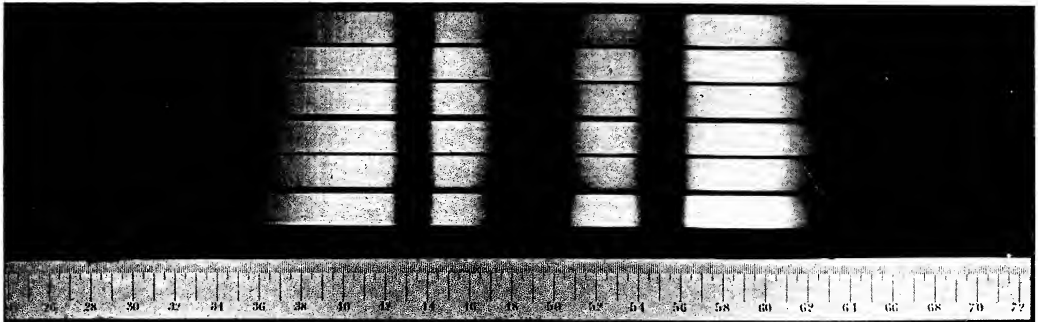
Plate XIX.

A


26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72

B


58 60 62 64 66 68 70 72

	Glycerol solution.	Methyl alcohol.	Ethyl alcohol.	Acetone.
a	5000	5000 (broad)	5000	5000 (weak)
b	4840	4815	4820	4840
c	4680	4650	4660	4680
d	4530 4440	4450 (very broad)	4460	4530 4450 weak
e	4310	4280	4280	4310
f	4170	4140	4140	4180
g	4050	4030	4030	4055

Uranous Chloride in Acetone, in Methyl Alcohol, and in Glycerol.

Plate XXII, *A*, represents the absorption spectra of a solution of uranous chloride in acetone, the depths of cell being 1.2, 2, 3, 5, 8 and 11.5 mm. The slit was 0.10 mm. in width, current in Nernst glower 0.94 ampere, exposure 1.5 minutes to glower and 3 minutes to the spark. The bands are faint and diffuse. By the addition of hydrochloric acid they are made very much stronger, although the wave length is not changed.

Plate XXII, *B*, represents the absorption spectra of uranous chloride in methyl alcohol, the depths of cell being 2, 4, 6, 8 and 12 mm. These solutions were made about six months before being used. Bands appear at λ 6650, λ 6200, λ 5600, λ 5250, λ 4900 to λ 5070, λ 4780, λ 4665, λ 4600, λ 4230, and λ 4110. The absorption is very strong throughout the region λ 4200, and is so general that there is hardly any banded appearance.

Plate XXII, *C*, represents the absorption of a solution of uranous chloride in glycerol containing strontium chloride. The depths of cell were 2, 4, 6, 8, 12 and 24 mm. The absorption spectra show the uranyl bands and the large uranyl blue-violet band. Besides these there is a diffuse band at λ 5300 and a band at λ 6200, which broadens rapidly as the depth of cell is increased. The uranyl bands are located as follows: *a*, λ 4980; *b*, λ 4840; *c*, λ 4680; *d*, λ 4445 (weak band at λ 4530); *e*, λ 4300, to *f*, λ 4170.

Uranous Chloride in Methyl Alcohol and Ether.

Two photographs were made, one of uranous chloride in methyl alcohol (next to the spark spectrum), and one of uranous chloride in a mixture of about 60 per cent. methyl alcohol and 40 per cent. ether. Further addition of ether caused a precipitate to be formed so that the absorption spectra could not be obtained.

The methyl alcohol solution showed complete ultraviolet absorption to λ 3700. The region λ 4300 showed considerable general absorption due to the blue-violet band. The following uranyl bands appear: *i*, at λ 3880; *h*, at λ 4000; *g*, composed of two bands, one at λ 4110 and a narrow band about 10 Ångström units wide at λ 4135; *f*, two bands, λ 4240 and λ 4285, the latter being quite narrow; *d* and *e*, one very broad band at about λ 4400; *c*, at λ 4610; and *b* at λ 4780. Two bands, λ 4930 (*a*) and λ 5050 are almost merged into each other.

The addition of ether caused the absorption to increase, the ultraviolet absorption extending to λ 3800 and the absorption from λ 4100 to λ 4450 being almost complete. The uranyl bands are slightly shifted towards the red. Their general character remains the same. The wave lengths are approximately: *i*, λ 3890; *h*, λ 4010; *g*, λ 4140; *f*, λ 4260; *de*, λ 4440; *c*, λ 4630; *b*, λ 4790; *a*, λ 4960, and a band at about λ 5050.

The effect of ether is to cause the bands to shift slightly to the red and to increase the amount of absorption.

Effect of the Presence of Acids on the Uranous Bands.

A spectrogram was made of a 3 mm. solution of 0.17 normal uranous chloride in water (strip 1). To this was added very strong hydrochloric acid until the depth of cell was 6 mm. (strip 2), and finally until it was 12.5 mm. (strip 3), and 24 mm. (strip 4).

The effect of hydrochloric acid is very marked. In general it shifts the uranyl and uranous bands to the red. It causes the uranyl bands to appear much stronger. In an aqueous solution the λ 6400 band is very broad, and the λ 6655 band comparatively narrow. Hydrochloric acid reverses the appearance of these two bands, shifting both towards the red at the same time. The following wave lengths give the effect of hydrochloric acid:

Plate XX.

A

B

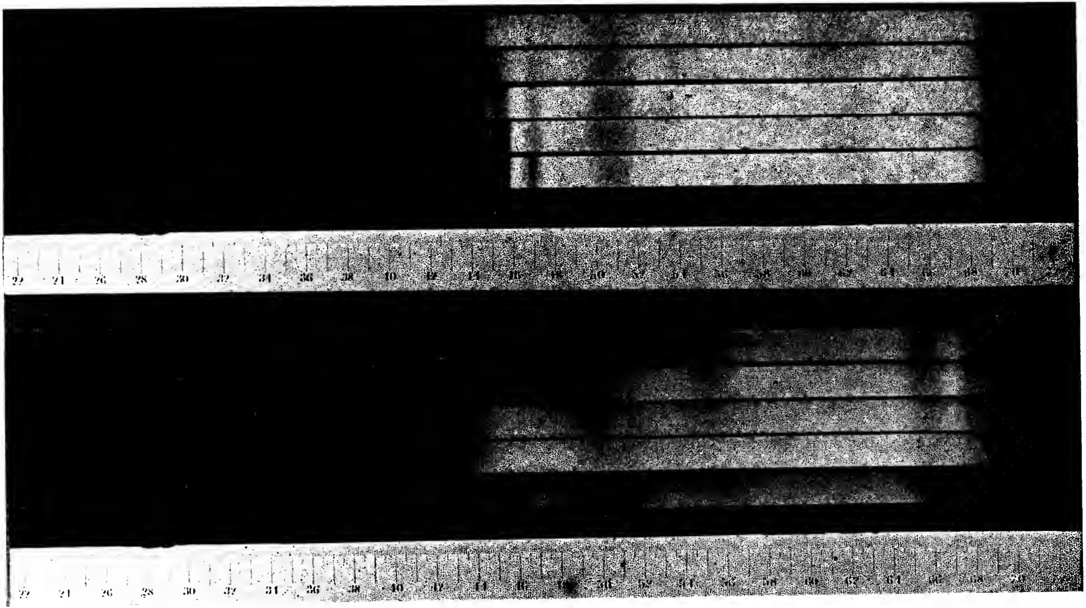

22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70
22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70

Plate XXI.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A


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B

	Strip 1.	Strip 2.		Strip 1.	Strip 2.
b	....	4800	*b*	4875	5000
c	....	4640	*c*	5520	5620
d	....	4490 (weak)	*d*	6340 (weak)	....
e	4380 (weak)	4420 (strong)	*e*	6430–6600	6500–6570
f	4280 (strong)	4280 (strong)	*f*	6755	6700–6850
g	4130	4150	*g*		

An aqueous solution of uranous chloride in concentrated hydrochloric acid gave the uranyl bands very distinctly. The uranium salt was reduced in this case in the presence of hydrochloric acid. The spectrum is almost identical with that of uranous chloride when hydrochloric acid is added after the reduction has taken place.

The addition of about 20 per cent. strong sulphuric acid to an aqueous solution of uranous and aluminium chlorides has a very marked effect upon the bands. The general effect is to shift the bands towards the violet. For the uranous chloride solution containing aluminium there is a band about 50 Ångström units wide at λ 6770 and a band from λ 6460 to λ 6640. These are the water bands. When sulphuric acid is added there is a wide band from λ 6600 to λ 6760, a narrow band at λ 6480, and a wide band running from λ 6200 to λ 6400. Sulphuric acid reverses the breadth of the two red water bands.

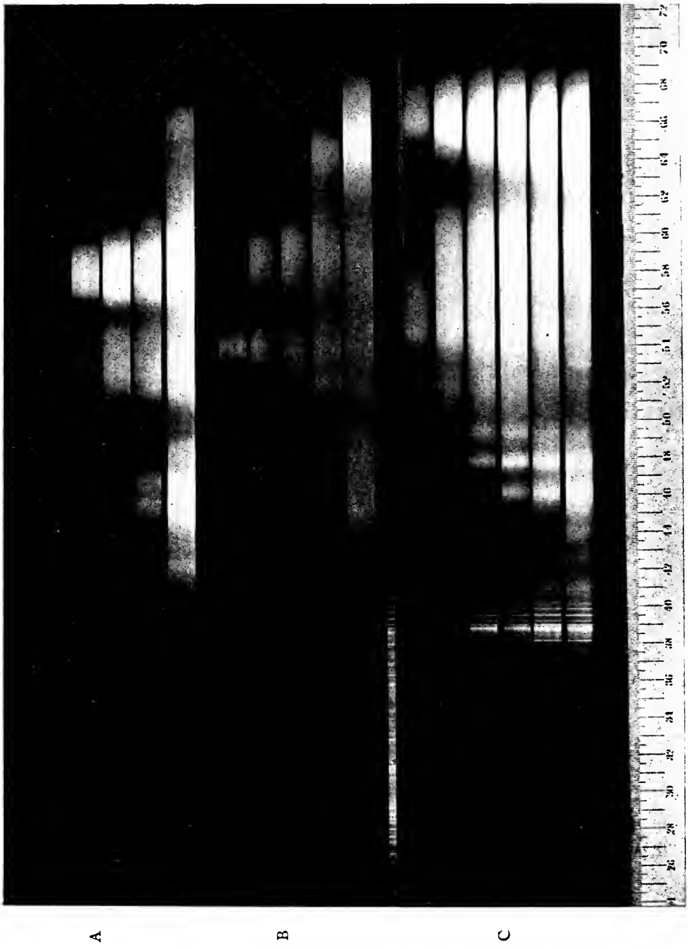
The water band at λ 5500 is shifted to the violet and doubled by the addition of sulphuric acid, the resulting bands being λ 5500 (strong) and λ 5400. The uranyl bands are all shifted to the violet as follows: *a*, λ 4990 to λ 4890; *b*, λ 4780 to λ 4750; *c*, λ 4620 to λ 4560; *d*, λ 4400 (λ 4490 weak) to λ 4360; *e*, λ 4280 to λ 4220; *f*, λ 4140 to λ 4080.

Uranous Chloride in Water and Methyl Alcohol; Water and Acetic Acid; Water and Nitric Acid; and in Water and Sulphuric Acid.

Strip 1, Plate XXIV, *B*, represents the absorption of a 4 mm. layer of a 0.17 normal aqueous solution of uranous chloride; strip 2, that of a solution whose depth has been increased to 6.3 mm. by adding methyl alcohol; strip 3, methyl alcohol added until the depth of layer is 7.5 mm.; strip 4, a 4

	Strip 1.	Methyl alcohol. Strip 3.	Acetic acid. Strip 5.	Nitric acid. Strip 6.	Sulphuric acid. Strip 7.
b	....	....	4785	....	4750 (very diffuse)
c	....	....	4620	....	4550 (very diffuse)
d	....	....	4450	....	4400
e	4380	....	4280–4245	4330 e?	4340
f	4280	4255	4130 *f*?	4240 *f*?	4220 (double narrow component on violet side)
g	4130	....	....	4120 *g*?	4100
	4875	4670 (characteristic)	....	4800 (very diffuse)	4900 (wide and strong)
	5520	5000 (very diffuse)	4900–5000	5450 (very diffuse)	5390–5490 (almost join)
	6340	5250 (very diffuse)	5500 (very diffuse)	6500 (50 A. U. wide)	6250–6380
		6200 (very diffuse)	....	6670–6760	6490 (30 A. U. wide)
	6420–6620	....	6450–6800	....	6610–6760 (quite well-defined)
	6755				

Plate XXII.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mm. layer of 0.17 normal aqueous solution of uranous chloride; strip 5 is the same as 4 to which acetic acid has been added to make the depth of layer 28 mm.; strip 6, a 4 mm. layer of 0.17 normal aqueous solution of uranous chloride, plus 2 mm. of strong nitric acid; strip 7, a 4 mm. layer of 0.17 normal aqueous solution of uranous chloride to which 19 mm. of sulphuric acid had been added.

Uranous Chloride to which Acetic Acid is Added.

Plate XXI, *B*, represents a slightly acid solution of uranous chloride in water to which is added glacial acetic acid until there is five times as much glacial acetic acid present as there was of the original solution. The addition of acetic acid causes a marked change in the absorption. The band *a*, λ 4980, doubles into the bands λ 5020 and λ 4930; *b* and *c* double without being changed very markedly; *d*, λ 4400, is slightly shifted to λ 4420; *e*, λ 4280 to λ 4300; *f*, λ 4140 to λ 4160; and *g*, λ 4010 to λ 4030; λ 5560 is shifted to λ 5590; λ 6450 to λ 6650 to λ 6500; and instead of the band at λ 6770 there are two bands λ 6650 and λ 6800.

Uranous Bromide.

Plate XIX, *A*, represents the absorption of an 0.8 mm. depth of 0.5 normal uranous bromide in water to which more and more water has been added. The depths of cell are 0.8, 2.8, 12.5, 22, and 35 mm.

The ultraviolet absorption is but slightly changed by the addition of water. The other uranous bands are narrower the greater the dilution of the uranous bromide. For the upper strip the positions of the bands are λ 4280, λ 4370 (these bands form practically a single band), λ 4850 (very diffuse), λ 4970 (these bands merge into each other), λ 5400 to λ 5600, λ 6200 to λ 6650 and λ 6750.

Uranyl and Uranous Acetates.

The action of free acetic acid upon the uranyl absorption bands of an aqueous solution of uranyl acetate is quite small. The bands are made quite narrow and weak. One spectrum gave *b*, λ 4730; *c*, λ 4610; *d*, λ 4470; *e*, λ 4330; and *f*, λ 4210.

This is very similar to the absorption spectra of the anhydrous salt. Uranous acetate in water (Plate XXIII, *B*) gives a lot of weak diffuse bands. The bands are located at *c*, λ 4600; *d*, λ 4460; *e*, 4330; *f*, λ 4200; and *g*, λ 4090. Besides these there are broad bands at λλ 5050, 5600, 6700, and 6850.

Absorption Spectrum of Dry Uranous Acetate.

The green precipitate that is formed when a solution of uranous acetate in methyl alcohol stands for several hours was illuminated by light from the Nernst glower, the illuminated salt being over the slit of the spectroscope. The green salt changed to a dark color, probably due to oxidation.

The absorption spectra showed weak diffuse bands at λλ 4240, 4350, 4500, 4650, and a wide band running from λ 4900 to λ 5200. If these bands are to be identified as the *f* (λ 4240), *e* (λ 4350), *d* (λ 4500) and the *c* (λ 4650) bands, and their relative intensities are about the same as that of the bands of uranous acetate in methyl alcohol, then the bands are slightly shifted towards the red, this shift being about 50 Angström units.

Uranous Acetate in Methyl Alcohol and Acetic Acid.

To a solution of uranyl acetate in methyl alcohol was added glacial acetic acid and some metallic zinc. The solution becomes green in color after standing a few minutes. In an hour or more a greenish precipitate is formed, and after standing several hours the solution shows only the uranyl bands. The plate represents the absorption spectra of the green uranous acetate. The only variation here is the depth of cell. For the three strips nearest the top the depth of cell was the same.

Starting in the ultraviolet the spectrogram shows a general absorption which extends into the blue for the greater depth of layer. No indication of the blue-violet uranyl band is to be noticed. Several fine bands appear in the blue-violet region. As these coincide very closely in position with the uranyl acetate bands they will be so considered. Of these the *a*, *b*, *c*, *d*, *e*, *f*, and *g* bands appear. The *g* band (λ 4070) is very faint. The *f* band (λ 4200) is stronger and is about

Plate XXIII.

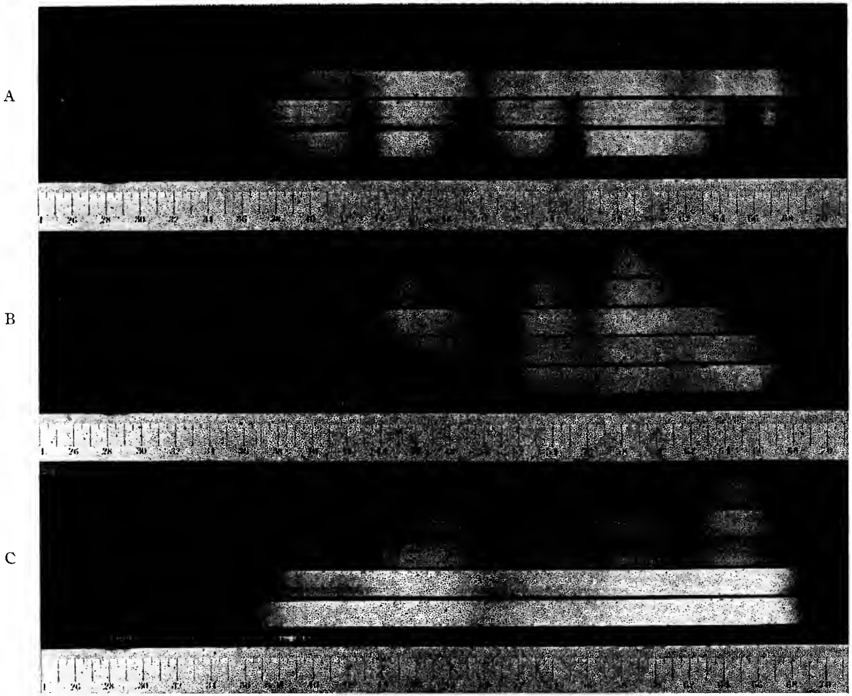
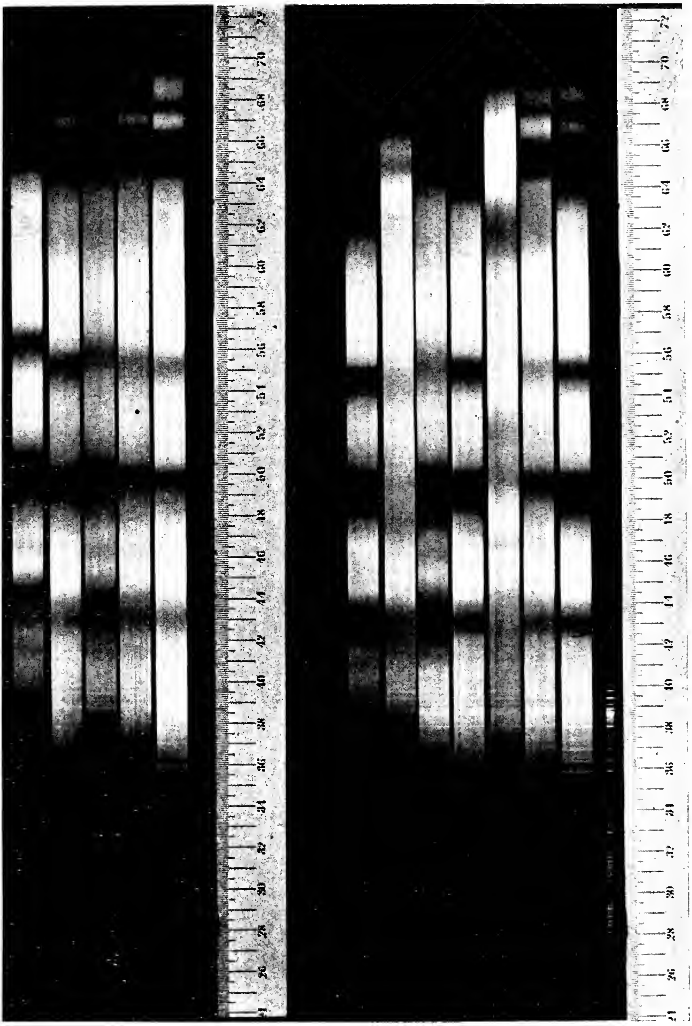


Plate XXIV.



A

B

30 Angström units wide. The *c*, *d*, *e*, and *f* bands appear quite strong, the *e* band being the strongest. It appears to be complex, being composed of a fuzzy band at λ 4285 about 10 Angström units wide; a fine sharp band at λ 4310 about 3 Angström units wide, and a band extending roughly from $\left\{\begin{matrix}\lambda\,4315\\ \lambda\,4316\end{matrix}\right\}$ to λ 4340. The *d* and *c* bands (λλ 4470 and 4610) are about 30 Angström units wide and of about equal intensity. The *a* and *b* bands are very weak (λλ 4910, 4740) and appear only on the original negative.

The *a* band with two other very diffuse bands λλ 5000, 5100 forms the wide absorption band in this region and the three practically merge into each other. A similar band extends from λ 5550 to λ 5650. In the red there are quite a number of fine bands very similar to the uranyl group in the blue and violet. These are very faint; the widest and strongest appears at λ 6450, this band being about 40 Angström units wide. The other bands are about 20 Angström units wide and are located approximately at λλ 6600, 6700, 6800, 6870, and 6920.

Uranous Acetate in Glycerol.

Uranous acetate was obtained as already described. Some of the solution in methyl alcohol and acetic acid was mixed with glycerol and warmed so as to drive off as much alcohol and acid as possible. The solution was filtered hot. The precipitate was green, the filtrate yellow, indicating that the uranium in the glycerol was mostly in the uranyl condition.

The absorption spectra showed several of the uranyl bands. These bands are not nearly so intense as the bands of uranous acetate in methyl alcohol and acetic acid. The *f* band λ 4220 appears to be double. The *e* band consists of a band about 15 Angström units wide at λ 4295, a band at λ 4340, and one at λ 4390; the *d* band, of two bands λ 4480 and λ 4530; and the *c* band, of λ 4630 and λ 4680, the latter being the weaker of the two bands.

The Wave Lengths of the Uranous and Uranyl Bands under Varying Conditions in Aqueous Solutions.

	Uranyl nitrate.	Uranyl chloride.	Uranous bromide.	Uranyl nitrate in HNO$_3$.	Uranous chloride.	Uranyl acetate.	Uranous acetate.	Uranyl bromide.	Uranyl acetate.	Uranyl sulphate.
a	4870	4920	4970 4880	4850	4980	4910	....	4880	4910	4900
b	4705	4740	4740	4670	4790 w	4740	....	4720	4740	4740
c	4550	4560	4600	4520	4550 w	4600	4600	4560	4595	4580
d	....	4460	....	4380	4420 w	4460	4460	4450	4455	4460
e	4310	4315	....	4240	4305 4270	4310	4330	4280	4310	4330
f	4155	4170	....	4140	4150	4160	4200	4160	4160	4200
g	4030	4025	....	4050	4020	4070	4090	....	4070	4070
h	3905	....	....	3920	3910	3970	....	....	3970	3970
i	3815	....	....	3810	....	3830	....	....	3830	3850
j	3710	....	....	3750	....	....	....	....	....	3740
k	3605	....	....	3670	....	....	....	....	....	3630
l	3515	....	....	3590	....	....	....	....	....	3530
m			6740	3520	5500	....	5050			
			6480	....	6500	....	5600			
			5500	....	6750	....	6700			
					6340	....	6850			

Alcoholic Solutions of Uranium Salts.

Uranous chloride in methyl alcohol gives bands at λλ 6650, 6250, 5600, 5260, 4900–5070, 4780, 4665, 4600, 4230, 4410.

Uranous bromide in methyl alcohol gives bands at λλ 6650, 6200, 5650–5500, 5250, 4950–5100, 4680S, 4450–4300, 4150.

	Uranous chloride in methyl alcohol.	Uranyl nitrate in methyl alcohol.	Uranons acetate in methyl alcohol.	Uranyl nitrate in ethyl alcohol.	Uranous chloride in ethyl alcohol.	Uranyl acetate in methyl alcohol.	Uranous bromide in methyl alcohol.	Uranyl chloride in methyl alcohol.	Uranous chloride in methyl alcohol.	Uranyl chloride in ethyl alcohol.	Uranous chloride in ethyl alcohol.
	5050	....	....	5000	5050 to	4880	5070	....	....	....	....
a	4930	4930	4910W	....	4950	4900	4900	4930	5000	4900	5000
b	4780	4760	4740W	4800	4710	4720	4780	4760	4815	4750	4820
c	4610	4610	4610	4630	....	4590	4665	4610	4650*b*	4580	4665
d *e*	4400*b*[1]	4455	4470	4475	....	4450	....	4465	4450	4400	4460
f	4285	4325	4330	4325	....	4320	....	4345	....	....	....
g	4135 4110	4190	4310 4285	4180	4290 W	4190	4230	4220	4280	4250	4280
h	4000	4070	4200	4080	....	4070	4110	4090	4140	4100	4140
i	....	3965	4070	3970	....	3980	....	3980	4030	3980	4030
j	....	3855	....	3875	....	....	....	3860 3760	....	3860	....
	5260	....	....	....	5280						
	6250	....	....	....	6250						

[1] *b* is broad.

Glycerol Solutions.

	Uranous acetate in glycerol.	Uranous bromide in glycerol.	Uranyl chloride in glycerol.	Uranyl chloride in glycerol.	Uranyl nitrate in glycerol.	Uranous sulphate in glycerol.	Uranous chloride in glycerol.	Uranous chloride in glycerol.
a	....	....	5060 w	5050	5040 5020	....	....	....
b	4680 4630 w[1]	...	4980 w 4840 s 80[2]	4900	4910 4750	$4780 + H_2SO_4$	5000 4790	5000 4840
c	4530 4480	4700?	4680 s 80	4720	....	4640	....	4680
d	4390 4340 4295	4550 w? 4430 w	4530 n.d.[3] 4440 w	4540 4400	....	4480	4550 4420	4530 w 4450
e	4220	....	4300	4260	4350	4365	4300	4310
f	....	4200?	4170	4140	4220	4250	4170	4260 w 10
g	....	....	4050 w	4025	4100	4120	4050	4170
h	....	....	3930 w	3920	3970	4010	....	....
i	....	....	3800 w	....	....	3900	....	....
j	....	....	....	....	....	....	....	....
k	....	....	....	....	....	3750	....	....
l	....	....	....	....	....	3650	....	....

[1] w means weak.

[2] s = strong, 80 = A. U.

[3] n. d. = narrow and diffuse.

Uranyl Salts in the Presence of Free Acid.

	Uranous chloride in water.	Uranous chloride with hydrochloric acid.	Uranyl acetate in acetone with acetic acid.	Uranyl acetate in water.	Uranyl acetate with acetic acid.	Uranous acetate in water.
a	4980	5000	....	4910	....	....
b	4790	4800	4620?	4740	4730	....
c	4550	4630	4460?	4595	4610	4600
d	4420	4430	4330?	4455	4470	4460
e	4305 4270	4270	4220?	4310	4330	4330
f	4150	4140	....	4160	4210	4200
g	4020	4020	....	4070	....	4030
h	3910	....	....	3970	....	....
				3830		
	6770					
	6550					
	5620					

Effect of the Presence of Foreign Salts.

	Uranyl chloride in water.	Uranyl chloride + $AlCl_3$.	Uranyl chloride + $ZnCl_2$.	Uranous chloride + $AlCl_3$.	Uranous chloride + H_2SO_4.
a	4920	4950	4930	4990	4890
b	4740	4790	4770	4780	4750
c	4560	4620	4600	4620	4560
d	4460	4480 to 4420	4400	4490 4400	4360
e	4315		4245	4280	4220
f	4170	4270	4115	4140	4080
g	4030	4135	....	....	....
h	....	4010	....	....	....
i	....	....	....	....	....

Effect of Free Acid.

	Uranyl nitrate in water	Uranyl nitrate to which H_2SO_4 is added.	Uranyl sulphate in water.	Dry uranyl nitrate in HNO_3.	Uranyl sulphate in H_2SO_4.	$UO_2(NO_3)_2.6H_2O$ in HNO_3.	Uranyl chloride in water.	Uranyl chloride + HCl.
a	4870	4925	4900	4850	4930	4790	4920	4950
b	4705	4750	4740	4670	4750	4670	4740	4800
c	4550	4560[1]	4580[1]	4520	4560[1]	4510	4560	4635
d	....	4380	4460	4380	4380	4370	4460	4480
e	4310	4240	4330	4240	4240	4230	4315	4420
f	4155	4100	4200	4140	4100	4125	4170	4280
g	4030	....	4070	4050	....	4000	4025	4050
h	3905	3980	3970	3920	3980	3900	....	4015
i	3815	3870	3850	3810	3870	3790		
j	3710	3770	3740	3750	3770	3670		
k	3605	3660	3630	3670	3660	3570		
l	3515	3560	3530	3590	3560			
				3520				

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[1] Double.

Any small differences in the wave lengths of the absorption bands of uranous solutions under different conditions are probably due to the presence of varying amounts of zinc used in reducing the uranyl to the uranous condition.

General Discussion of Results.

Previous investigators have in many instances spoken of the absorption of light by molecules, ions, or aggregates of these. At present, however, spectroscopists are more and more inclined to consider the negative electron as the chief absorber of light in the visible and ultraviolet portions of the spectrum. Whether the absorbing electron is the same as the electron found in vacuum discharge tubes, or emitted by radioactive elements, is at present a very much discussed subject. It seems to be quite certain that the masses of many of the absorbers are not of molecular magnitude. It is equally certain, as experiments show and as theory indicates, that the various coefficients which define the equations of motion of the absorber are *functions of the conditions under which the absorbers exist.* If the absorbers are electrons we may think of them as being within or in close proximity to the atom. Such absorbers would be expected to have their period, coefficient of damping and other coefficients, greatly modified by the formation of aggregates, solvates, *etc.*, and such seems to be the case. According to the present theory of the conductivity of solutions it would be expected that if the absorbers existed in or about the atom, their properties would be very greatly affected by the given atom existing in an ionic condition or as part of a molecule. Consequently, at great dilutions, it would be expected that the absorption of a colored solution of a salt would be entirely independent of the salt when the anion was the carrier of the absorbers. In the absorption spectra of solutions there are but few examples where the absorption spectra of different salts with the same cation are very different from each other. There is one important exception in the case of aqueous solutions of the uranyl salts. The uranyl nitrate bands are all of shorter wave lengths than the bands of the other uranyl salts. The absorption spectra of these salts have been photographed by us over quite wide ranges in concentration, and no evidence has been obtained that indicates any dependence of the wave lengths of the uranyl bands on the concentration.

Although more and more spectroscopic phenomena are being explained by means of the electron theory, yet there is a general tendency to consider that only the electrons in a few atoms are in a condition to absorb or emit light at any moment. The nature of these conditions is at present not well known, but it seems probable that they are *exceptional states*, in some cases at least. For instance, only a few of the sodium atoms take part in the absorption of the *D* lines at any particular time, and the same is probably true of neodymium and erbium salts in solution or in the solid state. It is supposed by some physicists that absorption or emission may take place during ionization, as, for example, when an electron leaves or returns to an ion. Upon a basis such as this are laid the theories of dynamic isomerism, isorepesis, and Stark's theory of the spectrum of canal rays and of fluorescence. On such a theory as this it may be supposed that in solutions the absorption takes place in those molecules that are undergoing dissociation, or in those ions that are combining to form molecules. In the case of the uranyl nitrate bands the combined action of water and the NO_3 group has a hypsochromous effect upon the wave lengths of these bands. That it is due to the combined action of the water and the NO_3 group is shown by the fact that in other solvents the NO_3 group does not have this hypsochromous effect; while in water it is only the nitrate bands that have the smaller wave lengths. According to the theory of dynamic ionization, the absorption of light could take place while the NO_3 groups were near the UO_2 group, so that the periodicity of the absorbed light would be affected. According to this theory, however, the number of ionizations through which a molecule would pass would probably be a function of the concentration; and thus the intensity of the absorption bands should be a function of the concentration. But for uranyl nitrate Beer's law holds at least approximately, whereas considerable variations would be expected from the above theory. If the absorption takes place during periods of ionization, and the intensity of the absorption depends only on the number of these ionizations, then the fact that Beer's law holds shows that the number of these ionization phenomena is independent of the concentration. The fact that the absorption spectrum of uranyl nitrate crystals is very similar to that of solutions indicates that the uranyl groups that take part in absorption are about as closely united with water and the NO_3 group in solution as they are in the solid.

It may, however, be said in general *that the anions of the various colored salts*—and in practically all cases it is the anion that exhibits banded absorption—*play a much less important rôle in modifying the spectra than the solvent.* Different salts of the same anion in the same solvent usually have the same absorption spectra. On the other hand, the absorption spectra of the powdered salts themselves may be very different. This fact shows that the *solvent plays a most important part in the absorption* and it *seems highly probable that in a large number of cases there is an "atmosphere" of the solvent molecules about the colored absorber. In a word, there is solvation.* However, in the case of the nitric oxide[1] spectrum it seems possible to have the gas existing in solution and at the same time having its absorption spectra unaffected. The nitric oxide spectrum occurs only under very special conditions, and has not thus far been obtained for solutions of the gas, but only when some acid is added to nitric acid or a nitrate.

Whereas the absorption of different salts of the same colored anion is in general very similar, on the other hand *the absorption spectra of the same salt in different solvents are often very different indeed.* Formerly this effect of the solvent was thought to be due to a difference in the value of the dielectric constant, but Jones and Anderson have pointed out that the most probable cause is the *formation of solvates, or more or less stable compounds of the salt and solvent.* The reason *for this conclusion is that in mixtures of two solvents, each set of*

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[1] Physic. Rev., **30**, 279 (1910).

solvent bands appears, the intensity of any solvent band being a function of the relative amounts of the solvents present. That these compounds or solvates have a definite composition seems to be indicated by the fact that for most of the neodymium, uranyl, and uranous salts there appears only a single set of "solvent" bands for each solvent; and in mixtures of these solvents in most cases but two sets of bands are necessary to explain the results. The persistence of solvent bands varies quite widely for the different solvents, and appears to be greatest for water and glycerol and less for the alcohols. The persistence of any one solvent band seems to be the same for quite widely different salts. There are, however, some cases where it may be possible that intermediate solvates are formed. The spectrum of neodymium chloride dissolved in mixtures of water and glycerol seems to indicate that the "water" band λ 4274 gradually shifts to the "glycerol" bands.

Probably no salts show more characteristic bands than some of the uranous salts in the various solvents: *water*, *the alcohols*, *acetone*, and *glycerol*. It seems probable that the absorbers are the same for the corresponding bands of any two "solvent" spectra. An important fact indicating this is given by Becquerel, who found the Zeeman effect to be the same when different solvents of the same salt were used. It is generally conceded that at higher temperatures solvates are broken up. At present, work is being done on solutions containing mixtures of two solvents in such proportion as to give both sets of solvent bands. As the critical temperature of one solvent is approached, according to the foregoing theory the bands of that particular solvent should disappear. In many cases the two sets of solvent bands differ not only in wave lengths but also in intensity and in the number of components. Of all the bands of the neodymium absorption spectra, the "water" band λ 4274 is one of the strongest and one that is freest from neighboring bands. Yet, in different solvents this band may become a doublet, a triplet, or may even apparently break up into a whole series of bands. It is quite certain that when the mechanism of these changes is known, our knowledge of chemical compounds will be increased very greatly, and it is very important that gradual changes of solvent or salt may be made at low temperatures where the bands are much sharper, and work is now in progress on this problem.

In some cases it is possible to break up the absorption bands by chemical methods into very fine bands. A very striking example is the case of uranyl and uranous salts in acetone solutions. The uranyl salt in acetone gives six bands in the region λ 5000 that are characteristic of acetone solutions. By the addition of hydrochloric acid to an acetone solution the uranyl bands are broken into fine components. Several of the uranyl bands become triplets and some doublets. But the most marked example is the addition of hydrochloric acid to an acetone solution of uranous chloride. Several very broad uranous bands are broken up into a number of very fine and quite intense bands.

One very interesting result has come to light from the examination of the effect of free nitric acid on the absorption spectra of uranyl nitrate; of sulphuric acid on the sulphate; acetic acid on the acetate; or hydrochloric acid, calcium or aluminium chloride on the chloride. In general, the *presence of these foreign reagents causes the uranyl bands to become more intense and, in most cases, narrower. The action of all the above reagents except nitric acid is to cause the uranyl bands to be shifted towards the red.* Nitric acid, however, causes large shifts towards the violet. The above reagents have a similar effect on the corresponding uranous bands.

The explanation of the above effects seems possible by supposing that aggregates are formed. In the case of neodymium salts the effect of the above reagents is very small, and nitric acid, instead of causing the neodymium nitrate bands to become narrower, stronger, and to be shifted towards the violet, simply causes the bands to become much more diffuse. The other reagents cause the neodymium bands to become diffuse, weaker, and to broaden somewhat towards the red.

In addition to trying the effect of acids upon uranium salts of the same acid, *spectrum photographs were made of the effect produced by adding acids to different uranyl, uranous,* and *neodymium salts.* Uranyl nitrate was treated with sulphuric, hydrochloric, and acetic acids; uranyl and uranous acetates with various acids; various uranous salts and neodymium acetate with nitric acid. These salts and acids were selected, since they showed the greatest spectroscopic changes. Especially interesting are the spectrograms of uranous salts treated with nitric acid.

The spectrophotographs of chemical reactions show, invariably, that the changes produced in the spectra as one salt is transformed into another are gradual, whereas in changing the solvent this is not the case. *For instance, when uranyl nitrate is transformed into uranyl sulphate, the uranyl nitrate bands gradually shift into the sulphate position.* The same effect is produced when solutions are made containing different amounts of uranyl nitrate and uranyl sulphate. Further addition of sulphuric acid causes the bands to shift still more. An example is given where to a small amount of a solution of uranyl nitrate in nitric acid a large amount of sulphuric acid is added.

	Nitrate in nitric acid.	Same plus sulphuric acid.		Nitrate in nitric acid.	Same plus sulphuric acid.
a	4850	4930	*h*	3920	3980
b	4670	4750	*i*	3810	3870
c	4520[1]	4560[2]	*j*	3750	3770
d	4380	4380	*k*	3670	3660
e	4240	4240	*l*	3590	3560
f	4140	4100			
g	4050				

It will be seen that the shifts in these cases are quite large, and the moving together of the *f* and *g* bands is especially remarkable. The chemical changes studied thus far spectroscopically have been, in most cases, confined to aqueous solutions. Changes effected in other solvents are usually smaller. For instance, the addition of sulphuric acid to a glycerol solution of uranous sulphate simply causes the *g*, *h*, and *i* bands to be shifted about 20 Angström units to the violet. Similar changes are often produced by adding salts containing the cation of the acid. For instance, it has been found

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[1] Narrow.

[2] Double.

that the absorption spectra of uranyl chloride in a concentrated aqueous solution of aluminium chloride, or zinc chloride, or hydrochloric acid, are very similar to those of uranyl and calcium chlorides in methyl alcohol, or of uranyl chloride in ethyl alcohol.

When nitric acid is added to an aqueous solution of uranous acetate, it is found that the oxidation of the uranous salt does not occur when small amounts of acid are added, but that in this case the uranous bands are shifted to the violet. The uranyl bands pass through several stages and change very greatly, indicating that the chemical reaction is quite complex.

The absorption spectra of uranous salts usually show the uranyl bands, and in some cases these are very strong. The question immediately arises as to whether the uranyl bands are common both to the uranyl and uranous salts. It seems probable that they are characteristic of only the uranyl salts, although this is not certain. Uranous salts have been obtained which show only a strong band appearing in about the same position as that of the blue-violet uranyl band, and this indicates that the presence of uranyl bands is due to the uranyl salt which has not been reduced. In most of the changes of solvent and salt it has been found possible to follow the individual uranyl bands throughout the reactions which took place, and this seems to indicate that the absorption is due to a system of some kind which preserves its entity throughout all these changes.

The gradual shift of the absorption bands as one salt of a metal is transformed into another salt by the addition of more and more free acid is very important.

In the reduction of uranyl salts to uranous salts it is very difficult to produce a complete transformation. As a result, most of the uranous salts show the uranyl bands, and probably on account of the presence of foreign salts or acids these uranyl bases often appear quite strong. In some cases, however, solutions of uranous salts were obtained which did not appear to have any uranyl bands in their absorption spectrum. Recently some spectrophotographs have been made of the oxidation of uranous into uranyl salts by the addition of small amounts of hydrogen dioxide. These spectrograms seem to indicate clearly that the "uranyl" bands in the region λ 3000 to λ 5000 are characteristic of the uranyl salts only.

Rise in temperature causes the general absorption of any salt in water to increase and also causes the bands to broaden and become more intense.

The increase in the general absorption with rise in temperature is much greater for concentrated solutions. This also holds true for bands of the second type, and to a small extent for bands of the third type.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge with rise in temperature.

The uranyl chloride bands are shifted towards the red with rise in temperature. No shift for the uranyl nitrate could be detected. Uranyl nitrate, however, dissolved in strong nitric acid showed quite a large shift. The uranyl acetate and sulphate bands were slightly shifted.

No shift with rise in temperature was noticed for solutions of neodymium or erbium salts. When calcium chloride is present the neodymium chloride bands are, however, shifted, and the remarkable fact is observed that the bands then become fainter with rise in temperature. This latter phenomenon is considered to be very important, and it may be that the abnormal Zeeman effect observed by Becquerel is due to the presence of foreign compounds in the tysonite and xenotin crystals.

When a neodymium salt is dissolved in water and alcohol in such a proportion that the "water" and "alcohol" bands are of equal intensity at a given temperature and a given concentration, it is found that these bands do not obey Beer's law.

Change of temperature[1] does not have the same effect upon the "water" and "alcohol" bands of a solution when these appear together.

One of the most important points brought out in this in-

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[1] Physik. Z., **11**, 668 (1910).

vestigation is the additional evidence furnished for the existence of solvates in solution, these solvates having very different compositions and very different spectra, depending upon the solvent in which the salt in question was dissolved.

It is not too much to say that by this work the whole solvate theory is placed upon a firmer basis.

This suggests the thought: Of what significance or scientific use is the solvate theory of solution?

Bearing of the Solvate Theory of Solution.

The evidence for the solvate theory of solution which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation has recently been brought together and briefly discussed.[1] The evidence is so unambiguous and convincing that ions and some molecules combine with more or less of the solvent that it can now be accepted as a fact of science.

This, however, raises a number of questions: What relation does the solvate theory of solution bear to the theory of electrolytic dissociation?

Does the solvate theory help us to explain any of the apparent discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general?

The Solvate Theory and the Theory of Electrolytic Dissociation.

When Arrhenius proposed the theory of electrolytic dissociation the question was not even raised as to the condition of the ions in the solution except that they behave as if they existed independently of one another in solution. The theory simply said that molecules of acids, bases and salts in the presence of a dissociating solvent like water break down to a greater or less extent into charged parts called ions, the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit

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[1] Z. physik. Chem., **74**, 325 (1910).

charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds, there being, however, some exceptions, as, notably, the halogen salts of mercury, cadmium and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation is so convincing that few chemists of any prominence who have carefully examined the evidence have ever doubted the general validity of the theory, and the theory has become substantiated by such an abundance of subsequently discovered facts that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry, and Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*, molecules for the most part being incapable of reacting chemically with molecules; and Nernst has shown that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and the solvent. At the time that the theory was proposed chemists did not know and probably had no means of finding out whether the ion is or is not combined with the solvent in contact with it. The solution of this problem remained for subsequent work.

Some of the many lines of evidence that ions and certain molecules are combined with a larger or smaller number of molecules of the solvent, and in many cases with a very large number of molecules of the solvent, have been recently discussed briefly by Jones in an article in the *Zeitschrift für physikalische Chemie.*[1]

The amount of the solvent combined with an ion is primarily a function of the nature of the ion or ions in the solution. It is, however, conditioned very largely by the dilution of the solution, and also by the temperature.

The evidence, some of which is given in the paper referred to above and the remainder in other publications of the results of investigations carried out in this laboratory during the past dozen years, shows that the power of the ions to combine with the solvent is by no means limited to water and aqueous solutions but is a property of solutions in general. The alcohols, acetone, glycerol,[2] *etc.*, combine with certain substances dissolved in them, and it seems more than probable that all solvents combine with the dissolved substances to a greater or less extent. In a word, we do not have simply a theory of hydration, but a theory of solvation in general, which is an essential part of any generalization which would take into account the facts presented by solution.

The solvate theory of solution has been regarded in some cases as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules and the former tells us what is the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

Does the Solvate Theory Help to Explain Any of the Apparent Exceptions to the Theory of Electrolytic Dissociation?

Given the theory of solvation in solution together with

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[1] "Evidence Obtained in This Laboratory during the Past 12 Years for the Solvate Theory of Solution." Z. physik. Chem., **74**, 325 (1910).

[2] "Conductivity and Viscosity in Mixed Solvents" by H. C. Jones and Coworkers. Carnegie Institution of Washington, Pub. No. 80.

that of electrolytic dissociation, the first question that arises is, does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed it was recognized and repeatedly pointed out that after all it is only a theory of "ideal solutions," *i. e.*, very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it often could not deal quantitatively with the very solutions with which we work in the laboratory.

The explanation of this shortcoming was not fully seen and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases," *i. e.*, dilute gases, but do not hold for gases of any considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

In the early days of the theory of electrolytic dissociation it was, however, pointed out that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases, and this was expressed in the equation of Van der Waals, while no analogous explanation was offered in the case of solutions.

That this point was well taken is obvious to any one. A theory of solution to be of the greatest value must be applicable to all solutions regardless of the nature of the substance, regardless of the nature of the solvent, and regardless of the concentration of the solution.

The explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that for solutions in general a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combination with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great even relatively to the total amount of solvent present can be seen from the following facts: In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three-normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water about five-eighths of the water present is combined with the dissolved substance, while in a two-normal solution about five-sixths of the water present is in a state of combination.[1]

What we suppose to be a normal solution of calcium chloride is, therefore, more than one and one-half times normal; while what we suppose to be a three-normal solution is in reality more than eight times normal. In the case of aluminium chloride, what we suppose to be a normal solution is more than twice normal, while what we prepare as a twice normal solution is about twelve times normal.

These few facts, taken from thousands of a similar character, show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation, while very concentrated solutions are many times more concentrated than, without the facts of solvation, we should be led to think.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred, and are much more concentrated than we are accustomed to consider from the amount of substance added to a given volume of the solution—more or less of the water present being in combination and only the remainder playing the rôle of solvent. Without the theory of solvation we have hitherto regarded all the water present as acting as solvent.

We should therefore not expect the laws of gases to apply to such solutions when we had no idea what their true concentration was. Now that we know their concentration we

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[1] "Hydrates in Aqueous Solution," by H. C. Jones and Coworkers. Carnegie Institution of Washington, Pub. No. 60.

find that the laws of gases are of as general applicability to solutions as to gases, holding not simply for dilute but also for concentrated solutions.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is then not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

Does the Solvate Theory Aid Us in Explaining the Facts of Chemistry in General and of Physical Chemistry in Particular?

To answer this question at all fully would lead us far beyond the scope of this paper. A few facts bearing upon this question can, however, be taken up. Take for example the action of the hydrogen ion both in the formation and the saponification of esters. In the presence of the alcohols the hydrogen accelerates greatly the velocity with which an ester is formed; while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions—the hydrogen ion under one set of conditions undoing what under other conditions it effected.

In terms of the solvation theory these reactions admit of a very simple interpretation. While the hydrogen ion is not strongly solvated, yet work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion plus the alcohol combined with it unites with the organic acid, forming complex alcoholated ions, which then break down, forming the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion, together with the water united with it, combines with the ester, forming a complex hydrated ion which then breaks down into the corresponding acid and alcohol, setting the hydrogen ion free again.

For a fuller discussion of this reaction see the paper by E. Emmet Reid.[1]

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[1] This Journal, **41**, 504 (1909).

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water, on the one hand, and of alcohol on the other. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion which then breaks down, yielding ammonia and acid, the ammonia, of course, combining with the acid.

In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion which then breaks down into ammonia and the ester of the acid in question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions simultaneously; but as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates, and under these conditions the first reaction proceeds much more rapidly than the second.[1]

A very large number of types of reactions could be discussed illustrating this same point, *i. e.*, the value of the solvate theory in interpreting chemical reactions.

When we turn to physical chemical processes the solvation of the ions has to be taken into account at every turn. The velocities of the ions are of course a function of the degree of their solvation, and the behavior of the ions, both chemically and physically, is a function of their velocities. The effect of dilution, and especially of temperature, on reaction velocities is largely a question of the velocities of the ions present, which, in turn, are a function of the degree of their solvation.

In determining the actual concentration of a solution the amount of the solvent combined with the ions must be taken into account, as has already been pointed out, and without knowing the actual concentrations of solutions quantitative chemistry would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the

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[1] THIS JOURNAL, **41**, 509 (1909).

conductivity of lithium salts is less than that of sodium and potassium, notwithstanding the fact that the lithium ion is much smaller and lighter than the atom of sodium and potassium. We now know that the lithium ion is much more hydrated than the ions of sodium and potassium, and the mass of the moving ion is really much greater than that of sodium or potass um.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity, and why dilute solutions have larger temperature coefficients of conductivity than concentrated solutions;[1] and we could multiply examples almost without limit, did space permit, of the effect of the solvate theory on physical chemistry.

Why is the Nature of Solutions of such Vital Importance not only for Chemistry but for Science in General?

The fact is well recognized that modern physical chemistry has reached out into nearly every branch of science and has had an important influence on many of them. The question arises: Why is this the case? The answer is that physical chemistry is primarily a science of solutions.

This answer may not at first sight appear to be self-evident, but a moment's thought will show its general correctness. The whole science of chemistry is primarily a science of solutions in the broad sense of that term. By solutions is meant not simply solutions in liquids as the solvent, but solutions in gases and in solids as well, and not simply solutions at ordinary temperatures but also at elevated temperatures. If we think of chemical reactions in general we will realize what a small percentage of them take place out of solution. Therefore, the nature of solution is absolutely fundamental for chemistry. This applies not simply to general chemistry, including

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[1] Jones: THIS JOURNAL, **35**, 445 (1906)

the chemistry of carbon, but also to physiological chemistry, which deals almost entirely with solutions in one solvent or another.

When we turn to physics we find solutions not playing as prominent a rôle as in chemistry, but nevertheless coming in many places. The primary cells, secondary cells, electrolysis, polarization, diffusion, viscosity, surface tension, are all phenomena in which the physicist is interested and all depend for their existence upon solution.

When we turn to the biological sciences we find that solution is almost as important as for chemistry. Take physiology —here we have to deal very largely with solution in the broad sense of that term. The same remark applies to physiological botany, and solutions are very important for both animal and vegetable morphology, especially in their experimental developments. Bacteriology is fundamentally connected with solutions, and pharmacology is based upon solutions either without or within the body of the animal.

Solution in the broad sense is as fundamental for geology as for chemistry. The igneous rocks were solutions of one molten mass in another, and sedimentary deposits came down for the most part from solutions in water. The minerals crystallized out from solutions, and solutions of various substances, such as carbon dioxide, are to-day weathering the rocks and continually changing the appearance of the face of the globe.

An examination of facts such as those referred to above will show the truth of the statement that the relation of physical chemistry to solutions is the prime reason why physical chemistry is so closely related to so many other branches of natural science.

This alone would show the importance of a true and comprehensive theory of solutions not alone for physical chemistry but for the natural sciences in general.

Description of Plates VIII to XXIV.

Plate VIII. *A.* Uranyl and Zinc Chlorides in Water.

Concentration of uranyl salt, 0.2 normal. Zinc salt, saturated.

Depth of cell, 3, 6, 12, 24 and 35 mm.

B. Uranyl Chloride and Hydrochloric Acid.
Concentration of uranyl chloride, 0.2 normal. Hydrochloric acid, very strong.
Depth of cell, 3, 6, 12, 24 and 35 mm.

Plate IX. *A*. Uranyl Chloride in Glycerol. Cell depth, 10 mm.
Concentrations, 0.176, 0.132, 0.088, 0.059, 0.041, 0.030, and 0.022 normal.

B. Uranyl Chloride in Glycerol. Cell depth, 5 mm.
Concentrations, 0.176, 0.132, 0.088, 0.058, 0.041, 0.03 and 0.022 normal.

Plate X. *A*. Uranous Bromide in Methyl Alcohol. Depth of cell, 3, 6, 11 and 16 mm.

B. Uranyl Nitrate in Water to which Hydrobromic Acid is Added.

C. Mixtures of Uranyl Nitrate and Uranyl Sulphate in Water.

	Strip 1.	Strip 2.	Strip 3.	Strip 4.	Strip 5.	Strip 6.
Uranyl nitrate (per cent.)	100	80	60	40	20	0
Uranyl sulphate "	0	20	40	60	80	100

Plate XI. *A*. Uranous Acetate to which Nitric Acid is Added.

B. The first four strips give the effect of adding hydrochloric acid to a nitric acid solution of uranyl nitrate. The remaining strips represent the same effect obtained by using a greater depth of cell.

Plate XII. *A*. Uranyl Nitrate to which Acetic Acid is Added.

B. Uranyl Nitrate in Water to which Sulphuric Acid is Added.
Cell depth, 8 mm.

Plate XIII. *A*. Uranyl Nitrate in Water to which Sulphuric Acid is Added.

B. Uranyl Nitrate in Water to which Acetic Acid is Added.

Plate XIV. *A*. Uranous Chloride in Water. Concentration constant. Cell depths, 1.2, 2, 4, 8, 16 and 32 mm.

B. Uranous and Aluminium Chlorides in Water.
Cell depths, 1.2, 2, 4, 8, 16 and 32 mm.

Plate XV. *A*. Uranous Chloride in Glycerol and Mixtures of Glycerol and Water. The first strip represents the absorption of a 6 mm. solution of uranous chloride in glycerol. Succeeding strips show the effect of the addition of water.

B. This is exactly similar to *A* except that methyl alcohol was added instead of water.

Plate XVI. *A*. Uranous Chloride in Methyl Alcohol. Concentration constant.

B. Uranous Acetate in Methyl Alcohol. Concentration constant.

C. Uranous Chloride in Glycerol. Concentration constant.

Cell depths, 3, 4, 6, 9, 13, 18 and 24 mm.

Plate XVII. *A.* Uranous Chloride in Acetone.

Cell depths, 5, 6, 8.3 and 15 mm. The first strip represents uranous chloride in acetone, and the following strips the same to which hydrochloric acid has been added.

B. In this case uranyl chloride instead of uranous chloride was used. Cell depths, 2, 3.4, 4, 5, 11 and 30 mm.

C. Strips 1, 2 and 3 represent the same effect as *A.*

Strip 4 represents an ether solution of uranous chloride.

Strips 5, 6 and 7 represent absorption of 2, 5 and 14 mm., respectively, of uranous chloride in acetone.

Plate XVIII. *A.* Uranous Bromide in Methyl Alcohol.

B. Uranous Acetate to which Nitric Acid is Added.

Plate XIX. *A.* Uranous Bromide in Water, Beer's Law Test. The first solution consisted of an 0.8 mm. layer to which water was added to make the depth 2.8, 6, 12.5, 22 and 35 mm.

B. Uranous Bromide in Glycerol, 0.06 normal concentration.

Cell depths, 5, 7.5, 10, 15, 20, 26 and 33 mm.

Plate XX. *A.* Uranyl Nitrate in Nitric Acid to which Sulphuric Acid is Added.

Cell depths, 8, 8.4, 9, 12 and 17 mm.

B. Uranous Acetate in Acetic Acid to which Hydrobromic Acid is Added.

Cell depths, 22, 22.3, 24, 30 and 36 mm.

Plate XXI. *A.* An Acid Solution of Uranous Chloride to which Ethyl Alcohol is Added.

Cell depths, 4.5, 5, 7, 15 and 35 mm.

B. Uranous Chloride in Water to which Acetic Acid is Added.

Depths of cell, 5, 5.8, 7.5 and 26 mm.

Plate XXII. *A.* Uranous Chloride in Acetone. Depth of cell varied.

B. Uranous Chloride in Methyl Alcohol.

Depths of cell, 2, 4, 6, 8 and 12 mm.

C. Uranous Chloride in Glycerol.

Depths of cell, 2, 4, 6, 8, 12 and 24 mm.

Plate XXIII. *A.* Uranous Chloride in Water to which Ethyl Alcohol is Added.

Cell depths, 3.2, 4.4, 6.4, 12 and 22.5 mm.

B. Uranous Acetate in Water.
Cell depths, 3, 6, 12, 24 and 35 mm.

C. Uranyl Acetate in Acetone and Acetic Acid.
Cell depths, 3, 6, 12, 24 and 35 mm.

Plate XXIV. *A.* Uranous Chloride to which Concentrated Aluminium Chloride is Added.

Strip 1, 3 mm. uranous chloride and 1 mm. aluminium chloride; strip 2, the same and 2 mm. aluminium chloride; strip 3, the same and 10 mm. aluminium chloride; strip 4 is a 3 mm. solution of uranous chloride; strip 5 is the same to which 13 mm. strong hydrochloric acid is added.

B. (1) Uranous chloride in water, 4 mm.; (2) plus methyl alcohol to 6.3 mm.; (3) plus methyl alcohol to 7.5 mm.; (4) uranous chloride in water, 4 mm.; (5) the same plus acetic acid to 28 mm.; (6) four mm. uranous chloride in water plus 2 mm. nitric acid; (7) four mm. uranous chloride in water plus 19 mm. sulphuric acid.

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PHYSICAL CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
October, 1910.

HELIX CHEMICA.

A STUDY OF THE PERIODIC RELATIONS OF THE ELEMENTS AND THEIR GRAPHIC REPRESENTATION.

By B. K. Emerson.

CHAPTER I.

Chancourtois, the first to propose a spiral arrangement of the elements in the order of their combining weights, was a geologist, and the writer has long used a modification of Crookes's double spiral[1] with students in geology in considering the "first things"—its first culmination in carbon, the vital element, its second in silicon, the earth element, and the iron-nickel group just below all having a peculiar suggestiveness.

The eccentric position of the Siamese-twin groups of the "eighth series" seemed an imperfection in Crookes's spiral and the writer was led to devise the helix described in this paper from a discussion of the subject with his colleague, Professor Hopkins, in which the latter explained the important valence-volume curve upon which he was working.[2]

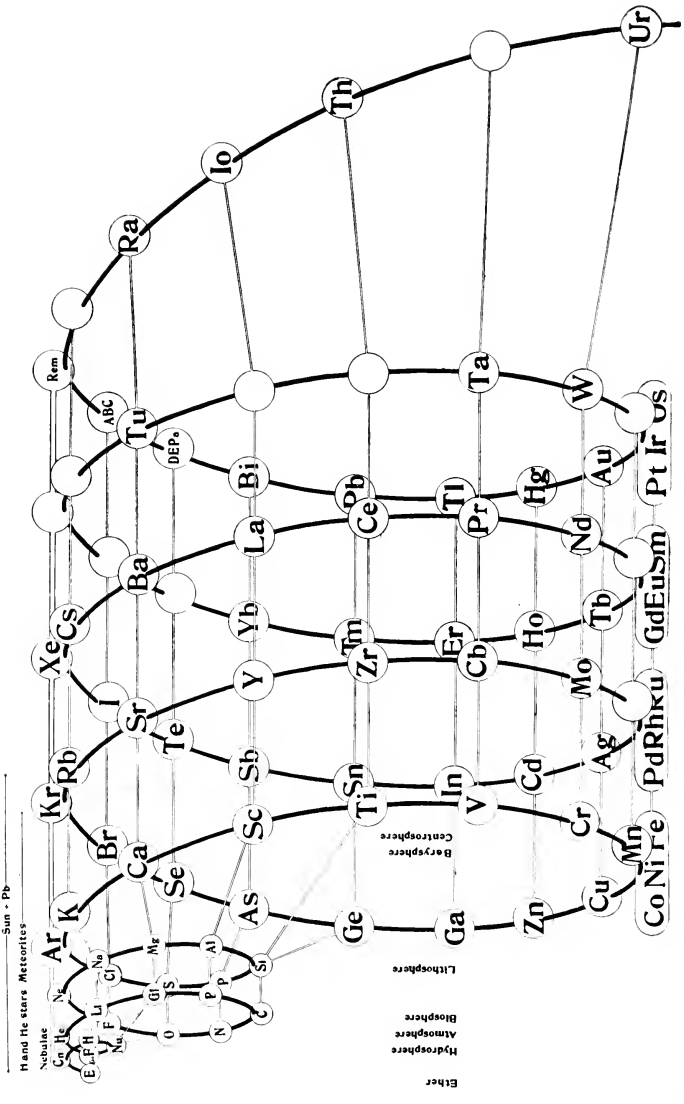
This curve emphasizes the important point that, while in the short periods the specific gravity rises from about 1 to 4, from lithium to carbon, or from sodium to silicon, and decreases to fluorine or chlorine, thus agreeing with the valence, from potassium through titanium, and in the later groups, the specific gravity rises parallel with the rise of the valence from 1 to 8.

From this came the idea of retaining the two short series in the old form of the Crookes spiral, with an amplitude of 4, or as octaves, and drawing the four long series with an amplitude of 8 as double octaves.

Very quickly the suggestion came to continue the curve backward to include hydrogen as a half-octave, preceded, finally, by a quarter-octave which ends at the origin of the

[1] Chem. News, **67**, 217 (1888).

[2] A. J. Hopkins: Science, **28**, 220 (1908.) Preliminary paper read at the Hanover meeting of the American Chemical Society, July, 1908.


Sun + Pb
H and He stars Meteorites
Nebulae
Ether
Hydrosphere
Atmosphere
Biosphere
Lithosphere
Barysphere
Centrosphere
Cn He
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Ne Li F
Ar Na Cl Gl O
K Mg S P N
Ca Se Al P Si C
Kr Br Sc As Ge
Rb Sr Te Ti Sn Ga
Xe I Y Sb V In Zn
Cs Sr Zr Cb Cd Cu
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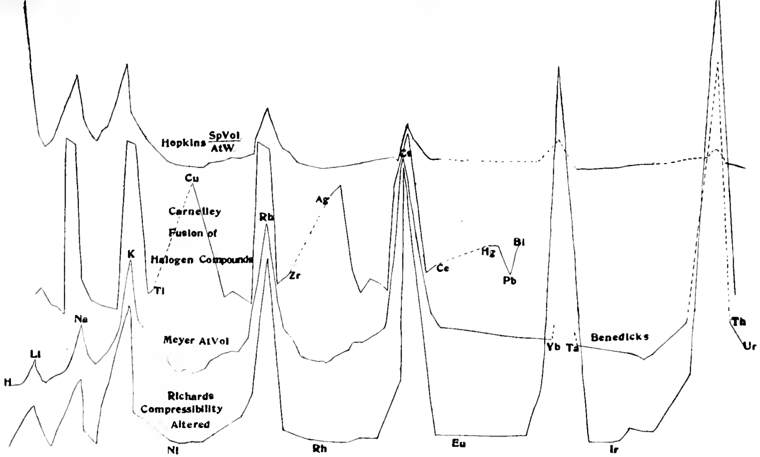

0	1/3	1/2	2/3	1	3/2	2	3		∞	Goldschmidts Law of Complication
	1/3	1/2	2/3	1	3/2	2	3			Law of Condensation $\frac{D}{V}$
	1/6	1/2	2/3	1	4/3	5/3	2	7/3		Vibration Period
	1/16	1/8	1/4	1	3/2	7/3				Refractivity

FIG. I.—A side view of the helix drawn to scale for me by A. L. Kimball, Jr. The four graphs below have been changed, in size only, to match the diagram. It will be seen that the apices of the same point exactly to the alkalis and match closely the four double octaves, the two octaves, and the half-octave. The table showing the longitudinal octave relations is placed below.

The atomic volume graph has been completed on Fig. V., in accordance with the calculation on page 184, and if the emended graph had been drawn its eight apices would have matched exactly the eight inert gases.

For fusion of halogen compounds see page 193; for Meyer's atomic-volume curve, page 183; for compressibility, page 186; for the law of complication and condensation, page 176; for vibration period, page 178; and for refractivity, pages 177, 195.

[In the text and the other figures accompanying this paper Proto F is used instead of Eka F.]

curve. In the other direction the helix was completed as a quadruple octave. The result was a spiral with increasing amplitude, in which all the loops are on one side and are drawn with a common axis passing through the line of the inert gases. In Figs. I and II this helix is represented from the side and in Fig. III it is drawn from the end. It is placed horizontally to bring the gases uppermost, the heaviest metals lowest, and so that the downward sweep of the curve is in the direction of the greatest compression. This brings it into a position harmonizing exactly with the curves of atomic volume, of specific volume, of compressibility, etc., as in Fig. I. In Fig. III*a* the same curve is drawn in a slightly false perspective: the four large circles which should really hide each other are drawn like four hoops on the end of a barrel, while the two smaller circles appear like hoops on a smaller barrel. This first free-hand curve I have not been able to improve materially, and so it has been copied on subsequent figures, as a background, on which to reproduce on a common scale many of the more intricate relations separately.

CHAPTER II.

The Helix.

1. The Origin.—At the origin of the curve is "der Urstoff," the "Protyle" of Bacon, the Ether or Electron, E, with valence and density equal to zero.[1] This is deduced below from the identity of the law of longitudinal condensation and the law of complication (see. p. 176). We may almost say, also, with an atomic weight of zero, since E is the x of Mendeléeff for which he deduced a hypothetical atomic weight one-millionth that of the hydrogen atom.[2]

It is difficult to discuss the elements without using language which indicates that they have been derived each from its predecessor. While this evolution has not been yet observed, the opposite devolution is exemplified in the derivatives of radium.

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[1] G. J. Storey: On Texture in Media and on the Nonexistence of Density in the Elemental Ether. Phil. Mag., [5] **29**, 467.

[2] Chemistry, English Edition, 1905.

We may thus take ether to be not an element but the origin of all the elements.

2. *The Initial Half-Circle.*—The curve rising from ether to coronium (see Figs. I and III) represents by its length and direction the passage of a group of ultimate corpuscles or electrons into a simplest element. Its length is proportional to the atomic weight of coronium; its direction indicates expansion.

Coronium present in the corona of the sun is drafted into this first position since it is supposed to be a very light and inert gas.[1]

There is spectroscopic evidence that coronium has a lower atomic weight than hydrogen, for the lines due to its presence in the solar gases can be observed further from the sun than those of hydrogen.[2]

It must have, from its position in the row of the inert gases on the helix, a valence equal to zero and a specific gravity that permits it to be condensed into hydrogen, whose specific gravity is 0.086. Its refractive index may be about 36 (see page 178).

It occupies the position of the second element y extrapolated by Mendeléeff,[3] for which he obtains a possible atomic weight of 0.4. By the same method, but taking closer account of the change in the ratios (which are enclosed in brackets in the table below), we obtain the value 0.3.

$$\frac{\mathrm{Ca}}{\mathrm{Mg}} = 1.6 \ (1.1) \ \frac{\mathrm{K}}{\mathrm{Na}} = 1.7 \ (1.2) \ \frac{\mathrm{Ar}}{\mathrm{Ne}} = 2$$

$$\frac{\mathrm{Mg}}{\mathrm{Gl}} = 2.67 \ (1.2) \ \frac{\mathrm{Na}}{\mathrm{Li}} = 3.28 \ (1.5) \ \frac{\mathrm{Ne}}{\mathrm{He}} = 5$$

$$\frac{\mathrm{Li}}{\mathrm{H}} = 7 \ (1.9) \ \frac{\mathrm{He}}{y} = 13.3 \ y = 0.3$$

The symmetry of the helix would suggest a still smaller number near zero (see page 168). The position of coronium is a

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[1] See G. F. Becker: Relations of Radio-Activity to Cosmogony. Bull. Geol. Soc. Am., **19**, 125 (1908).

[2] A. E. Garrett: The Periodic Law (1909), p. 243.

[3] Chemistry, English Edition, 1905. A. E. Garrett: The Periodic Law (1909), p. 241

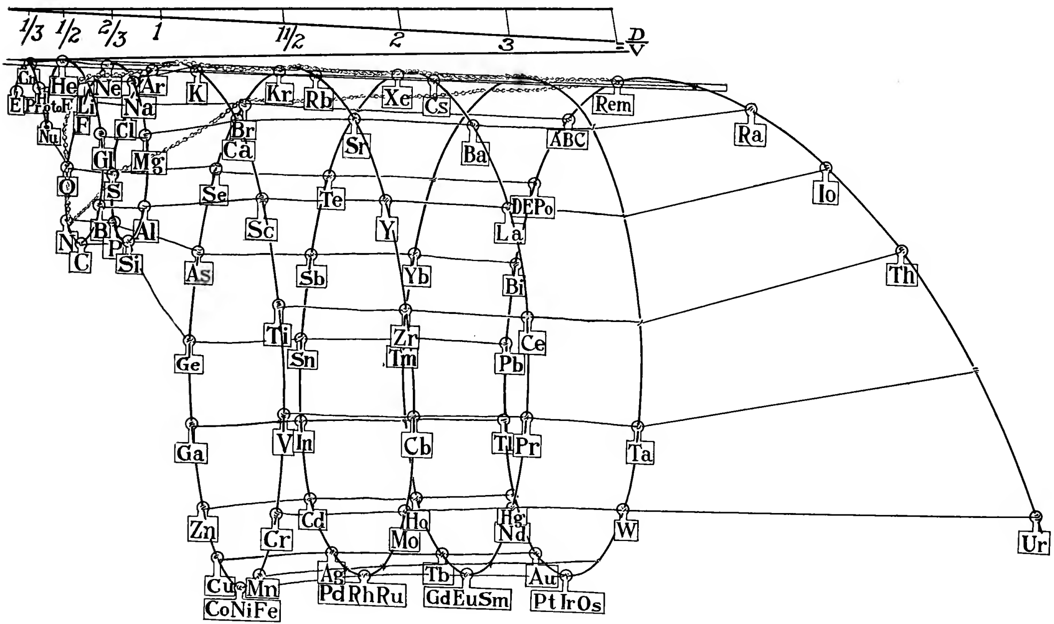
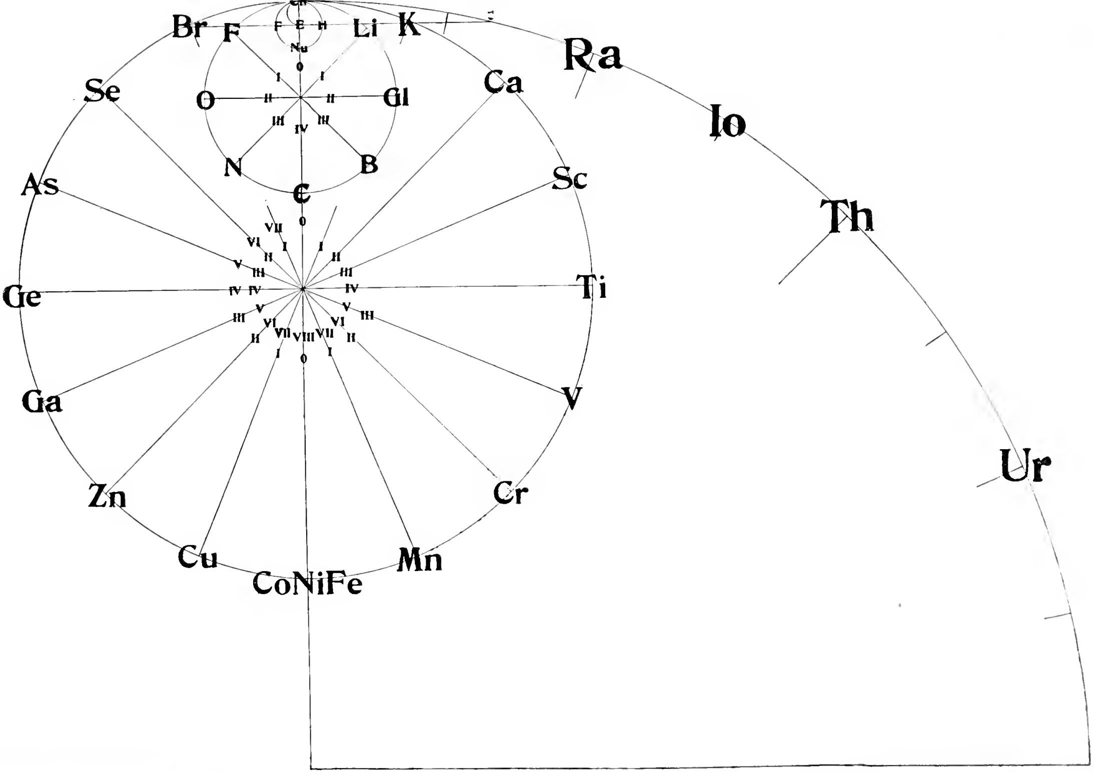


FIG. II.—From a photograph of a model of the helix constructed for me by A. L. Kimball, Jr., and R. D. Eaglesfield.

A chain is placed at the lower boundary of the gas area, but the camera had to be so placed to prevent the letters overlapping that it is not well seen. The front half is concealed by the rod. It can be seen to pass in front of Ar, Ne and He, then to bend down to include F, O and N, and then to rise in the rear of the figure to graze Br.

The model is depressed to the right to bring this chain into the horizontal position of a contour line. The amount of this depression is indicated by the acute angle placed above the diagram, and the numbers represent the longi-



F
E
H
Nu
Br
F
Li
K
O
Gl
N
B
C
Se
As
Ge
Ga
Zn
Cu
CoNiFe
Mn
Cr
V
Ti
Sc
Ca
Ra
Io
Th
Ur
0
I
II
III
IV
V
VI
VII
VIII

culminating point where the curve passes through zero, and all that is implied by this in mathematics is realized in Nature at this and the subsequent similar passages.

Dilatation and all its consequences are followed symmetrically by condensation and all its consequences.

We may distinguish three possibilities at this point:

1. As water rises in a wave and sinks back into itself, so the coronium formed from the ether might continuously sink back into the ether again. This would be typified by a closed circle with a single vertical diameter, with coronium at the top and ether at the bottom.

2. We may assume the third dimension to enter into the curve and the latter to complete itself without touching the point of origin, and to become a simple helix of this amplitude. The next element produced at the bottom of the curve would have been a monad and there would have followed an alternating succession of monads and nullivalent elements.

This represents a possible condition of a simplest nebula.

3. The Second Circle.—The simple possibilities suggested in the last section were not realized, but in sinking to greater condensation from coronium to hydrogen the passage is along a curve of double amplitude. This curve is drawn by taking the curve coronium-hydrogen equal to unity. This is best shown in Fig. III. This second curve is a half-octave bisected by two diameters, horizontal and vertical, giving places at their ends for four elements.

It is as if an added momentum had increased the tangential component of the curve and so extended the circle. This recalls the curious theory of a German chemist, which I have read but cannot locate, that valence depends upon the angle of impact of the elements in combining.

There is a certain completeness in the symmetry which makes the first complete circle quadrated, with four elements at the ends of the diameters, whose combining weights are 1, 2, 3, and 4. At the end of the first quadrant, on the electropositive side, stands hydrogen with the combining weight 1. At the end of the second quadrant must stand a dyad with the combining weight 2. Nebulium, which appears in the nebulae, is supposed to be somewhat heavier than hydrogen, since it has been found to be more concentrated in the central parts of a nebula than hydrogen,[1] and may stand here. At the third quadrant there must be a univalent element with the combining weight 3, and strongly electronegative. Here I have written protofluorine, since, as the diagram shows, this element stands above fluorine at the head of the halogens. Perhaps it may be among the new constituents of unknown nature found in Uranus and Neptune.[2] It is true of the octaves which follow that the combining weight of an element is always 16 less than that of the element below it; thus, as the combining weight of lithium, 7, may be derived from that of sodium by subtracting 16 from 23, so the combining weight of protofluorine may be obtained from that of fluorine: $19 - 16 = 3$.

At the end of the fourth quadrant stands helium with the combining weight 4, valence 0, occupying the second zero point.

The argument for the existence of such a half-octave is cumulative, and must appear mainly in the subsequent pages and from an inspection of the diagram. Anticipating, it will be seen that there are four double octaves containing sixteen elements each, two octaves containing eight elements each, and this demands one half-octave containing four elements, and the half of a quarter-octave containing one element. This interesting symmetry is more fully explained in Section 7, page 168. An inspection of the curves of atomic volume, of specific volume, and of compressibility (see Fig. I) will show that there are four loops corresponding to the four double octaves, two of half-width like the octaves, and one space of half the latter width remaining for the half-octave. This incorporates Mendeléeff's suggestion of a series including hydrogen, but makes it a short or half-series in which an intensified fluorine alone remains to be discovered.

The distance advanced along the first circle is four (helium = 4), and since four elements find place in this circle the inter-

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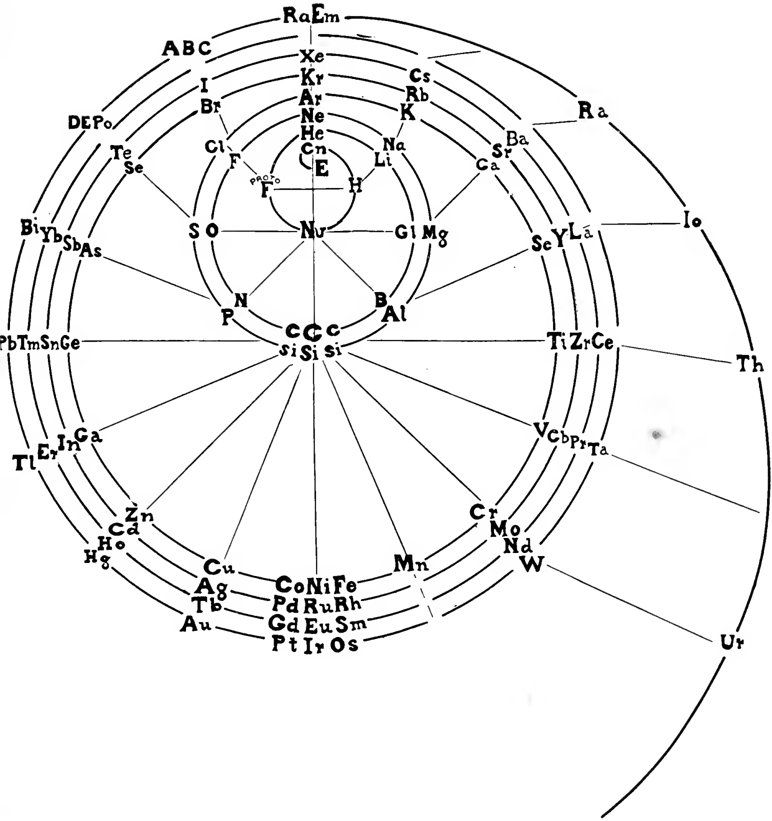
[1] Svante Arrhenius: Das Werden der Welten (1908), p. 177.

[2] *Loc. cit.*, p. 55.



IG. III*a*.—The helix drawn in false perspective so that the octave rings appear like hoops on the end of a barrel; the double octaves like hoops on a larger barrel.

The outer rings are about in the true ratio of 0:1:2:3:4. The groups of Mendeléeff are placed radially; the series along the curve. The curve E-Cn is an infinitesimal and E is almost in the line of the inert gases.

[NOTE.—Copies of this figure may be obtained from the Editor.]

space coronium-hydrogen is one, and the quadrant of this circle has been drawn as unity. We may anticipate the fact that these interspaces average successively 1, 2, 3, 4 for the different groups of circles. These interspaces are really the graphic representations of interweights, and seem to indicate in the half-octave the continuous addition of an assemblage of corpuscles about equal to a unit (or hydrogen) atom; in the octaves the continuous addition of a group equivalent to a dyad (a nebulium atom); in the double octave the continuous addition of a triad (protofluorine atom); and in the outer or radium circle the continuous addition of a quadrivalent (helium) atom, just as the giving off of an α particle is a subtraction of the equivalent of the same helium atom.[1] So perfectly is the half-octave a microcosm suggesting the evolution of the whole series. If the helix had gone on with this amplitude a fourfold succession of elements might have been made with the maximum valence 2. This we may call the nebula condition. See Fig 1, top.

There is some spectroscopic evidence for the existence and proposed arrangement of the half-octave. Of the very simple spectra detected in the simplest nebulae, the lines with wave length 4340 t.m. and 4862 t.m. have been found to belong to hydrogen. The name nebulium has been given to the element showing the next line, 4857 t.m. The next higher number, 5007 t.m., may be tentatively assigned to protofluorine, and the still higher number, 5876 t.m., belongs to helium.[2]

4. *The Construction of the Octave Circles.*—Following the one half-octave come two octaves. In these the elements sink in wonderful symmetry through lithium to carbon and rise through fluorine to neon. They repeat this curve with absolute fidelity through sodium to silicon and on through chlorine to argon. The valence changes from one in the alkalis to two in the alkaline earths, and then on to a maximum of four in carbon and silicon. It decreases regularly

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[1] Professor J. J. Thompson accepts the view "that it is by the combination of the atoms of the lighter elements that the atoms of the heavier elements are produced" (Electricity and Matter, p. 126).

[2] A. C. and A. E. Jessup: Evolution and Devolution. Phil. Mag., [6] **15**, 29.

on the upward curve to one in the halogens. Hopkins has insisted on the importance of the fact that the specific gravity is about one in the monads, and rises symmetrically to about four in the tetrads, sinking again regularly in all the solid elements, parallel with the valence.

To form the first octave, we follow along the curve from helium past lithium, and find it completed in neon, and the length of the curve is 16 [Ne (20)—He(4) = 16]. The curve is repeated past sodium to argon, and this distance is also 16. This is the reason for the constant difference of 16 in the combining weights of adjacent elements of the first two series. Since there are eight elements along each of these curves, the length of the interspaces must average two (16/8). Therefore the distance helium-lithium is made twice as great as the unit coronium-hydrogen in the first circle. As the first circle was cut by one diameter and the second by two, these are cut by four diameters, giving place for the eight elements found upon each. Here again the series of circles might have continued indefinitely, making symmetrical octaves with a maximum valence of 4.

5. The Construction of the Double Octaves.—When we come to the potassium-calcium circle, there is a radical change. The first four elements are exactly comparable with the first four elements of the two preceding octaves, potassium with sodium, calcium with magnesium, and so on. Valence and specific gravity are also exactly comparable, rising from one in potassium to four in titanium, but the specific gravity and one of the valences continue to increase, reaching each a culmination of eight in the iron group and growing smaller through copper to one in bromine and zero in krypton. This is repeated four times, the elements sinking in a curve of doubled amplitude and frothing four times into a triad group like the spray on the crest of a great wave. Each triad group occupies the place of a single element. It is interesting that carbon and silicon, at the crests of the octaves, by their three marked allotropic forms prophesy these triads at the crests of the double octaves.[1]

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[1] J. Emerson Reynolds: Nature, **81**, 206 (1909).

The length of each of these circles, though slightly less regular, is about forty-eight (Sr — Ca = 48, Ba — Sr = 49, etc., etc.). As we drew four diameters in the last circles, we must draw eight here, making places at their ends for sixteen elements in each circle, and sixteen elements are found for these places. The interspace (which was one in the first circle and two in the second circle) here becomes three (48/16).[1]

Since *one* half-octave and *two* octaves are present there should be *four* double octaves, and four are found, nearly complete and symmetrical, beginning with potassium and ending with the radium emanation, Ra Em, which is placed here tentatively, as are the other radium derivatives.[2]

6. The Quadruple Octave.—The symmetry which limits the number of the preceding double octaves to four is a principal argument for postulating a quadruple octave for the radiant elements. Moreover, the average interspace or change of weight is almost exactly four, completing the series of interspace numbers 1–2–3–4, and the α particles have an atomic weight of four.

The elements of the half-octave are sufficiently peculiar. They are the nebulae makers. Hydrogen has been a waif and stray ever since the periodic system was proposed. The octave elements have long been isolated as the "normal elements," and the double octave elements have, especially in the higher valence semicircle, many common peculiarities. In the same way, the few elements that represent the still larger circle are separated by their spontaneous decomposition, their high combining weight, and in many other ways, from the preceding groups.

As we drew eight diameters in the last circle we must draw sixteen here, and we may assume that thirty-two elements would normally find place on one of these circles at the ends of these diameters, and as the number of the circles has increased in geometrical progression the number of these larger circles should be eight.

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[1] The line of the curve runs through the rare elements with great uncertainty, like the broken line of history through the dark ages, when there was more alchemy than chemistry.

[2] Newly called Niton, atomic weight 221. Nature, **1910**, 517.

The helix is thus a multiple series of circles increasing *per saltum*, beginning with an origin at E and continuing *ad infinitum*; but in the last group only the first quadrant of the first circle is present, the helix being limited in this direction by the great complexity of the atom, which falls apart spontaneously; just as the schoolmen explained that there were no animals larger than the elephant, because, if they had been created, they would have collapsed of their own weight.

7. *Tabular Representation of the Symmetries of the Helix.*—The symmetrical relations of the helix which have been explained in the preceding pages are brought together in the following table. These relations have been deduced directly from the atomic weights and the recurring similarities of the elements. The ideal serial positions of the elements are found to be symbolized by the simplest harmonic relations of the simplest increasing series of circles.[1]

As the atomic weights of the elements have been found not to be whole numbers, so the interweights which are represented by the interspaces in Column 1 would not be whole numbers but close averages, and the first one would not be zero, but some very small number. See p. 162.

It is interesting that while the lengths of the interspaces are in the simplest arithmetical ratio, all the other relations are in the same simplest geometrical ratio, *viz.*, the number of interspaces, the number of circles, and, if we consider ether an element, the number of elements in each circle; while the length of the circles is obtained by combining these two ratios.

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[1] As the last circle is so incompletely represented, it was not at first apparent what was the continuation of the curve, and three other alternatives were considered; and it is interesting to present them for comparison with the chosen arrangement, which seems to be the true one.

In one case the last half-curve containing uranium was supposed to be identical with the preceding ones. This ignores the regular progression (which would demand four double octaves only) and the increased interspace.

A second case was suggested by the fact that radium, thorium, and uranium occupy every other space, making possible an octave (that is, eight elements) on a fifth circle of the same size as the preceding one, followed by a circle of the same size on which every fourth space was occupied. The location of ionium militates against this.

A final case suggests an arrangement of too ideal symmetry, where the coil ends as it begins; with two octaves followed by one half-octave. It brings uranium round into the electronegative position.

	Quarter-octave.	Half-octave.	Octaves.	Double octaves.	Quadruple octaves.	
(1) Length of interspace (= interweights) in each type of circle (approximate). Unit curve = Cn—H	0	1	2	3	4	Simplest arithmetical ratio.
(2) Number of interspaces in each type of circle	2	4	8	16	32	Simplest geometrical ratio.
(3) Number of elements in each type of circle	2	4	8	16	32	
(4) Number of circles of each type	1/2	1	2	4	8	
(5) Number of elements in each circle, obtained from (4) and (2)	1	4	8	16	32	
(6) Length of each type of circle, obtained by multiplying preceding ratios in (1) and (2)	0	4	16	48	128	Combination of above.

8. As to the Length of the Axis of the Helix.—It is natural to think of the helix as a real entity and to ask what is the distance between the successive curves. Indeed, I have spoken above of the third dimension asserting itself, so that the second circle did not coincide with the first and so formed a helix, instead of a flat spiral. As an expression of the symmetries concerned, there must be at least an infinitesimal distance between these curves.

The conditions imposed by the numbers in the preceding table would seem not to fix this distance. If we imagine the wire of the helix in Fig. II to be pierced with holes through which the axis runs, the helix could be drawn out or compressed by sliding along the axis, without disturbing the relations expressed in the above table.

The model in Fig. II was constructed by giving a convenient length to the distances between the double octaves, and half and a fourth of that for the whole and half-octaves. It would be perhaps best to have these distances proportional to the differences between the atomic weights of the elements located along the axis, though this relation has also been used to determine the length of the circles.

9. *Atomic Weight Differences as Evidence of the Correctness of the Proposed Arrangement.*—Pettenkofer's suggestion of the constant differences between analogous elements finds such full expansion and explanation when applied to the present arrangement as to form a practical proof of the correctness of the arrangement itself.

In the octaves there is a constant difference of sixteen (Si — C = 16, Ne — He = 16, etc.), and in the double series a constant difference averaging close to forty-eight. In passing through potassium and calcium the circles diverge and the differences gradually increase from 16 to 48 (K — Na = 16, Ca — Mg = 17, Co — Si = 30, Br — Cl = 45). An inspection of the diagram (Fig. III*a*) shows the reason for this increase to be as follows: While from neon around to argon the distance is wholly in the smaller circle (16), and from argon to krypton wholly in the larger (48), any subtraction made between members of the second octave (the sodium series) and the first double octave (the potassium series) will be measured in part on the short circle and in part on the long circle, and so will give a succession of numbers increasing from sixteen to forty-eight, as the distance passes entirely to the long circle. It will be seen that the increasing distance in the diagram between the half-octave and the octave, and between the octave and the double octave, is exactly parallel to the differences in the atomic weights of the corresponding pairs of elements.

The results reached from the smaller circle, although partly surmise, are of curious interest. Starting from H = 1, we assume Nu = 2, as it gives indications of being heavier than hydrogen, and Proto F = 3 [F(19) — 16 = 3] and find He = 4. This gives the proper difference, 16, for F — Proto F, and the difference decreases regularly (O — Nu = 14, N — Nu = 12, C — Nu = 10, B — Nu = 9, Gl — Nu = 7) until we find Li — H = 6, and the assumption for coronium of a very small fractional combining weight would make He — Cn near 4.[1]

A further inspection of Fig. III*a* would suggest that if Ne — He = 16, F — Proto F should be less than 16, but a comparison with Fig. X will show that the undue symmetry of the diagram is here misleading, and that in reality fluorine and all the halogens are placed so near the inert gases that the distance would be near 16.

Finally, if the last circle were of the same dimensions as the preceding, the atomic weight differences between elements in the same horizontal series would still be 48. If the circle is enlarged and the normal interspace between successive elements along the circle is four instead of three, each difference after passing the zero line at radium emanation should be increased by one unit because of the increased interspaces. It will be seen from the table below that the observed differences are closely what would be expected with the enlarged circle:

Elements in fifth circle	Ra Em	..	Ra	Io	Th	....	Ur
Corresponding elements in fourth circle	....	..	..	..	..	....	Ta
Ideal differences with the last, or fifth, circle of the same size as the four preceding ones	48	48	48	48	48	48	48
Ideal differences with enlarged fifth circle	48	49	50	51	52	53	54
Observed and calculated differences	48	47	55	52	52	52·5	54·5

The most probable values of the atomic weights, obtained by adding 3 to the corresponding element on the third circle, were taken for the unknown elements in the lower row, and subtracted from those of the elements in the upper row to

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[1] This makes the position of hydrogen at the head of the alkalis more probable than at the head of the halogens, and at the same time approximates hydrogen and protofluorine so closely, and so entirely without the possibility of an intervening element ("E" is not an element) that the question becomes a subordinate one in a certain sense.

Hydrogen is also electropositive, and so more naturally at the head of the alkalis.

See Orme Masson (Chem. News, **73**, 283) who marshals the arguments in favor of placing hydrogen at the head of the halogens.

obtain the observed differences given, except, of course, in the case of uranium—tantalum, and the result agrees quite exactly with the assumption of an enlarged circle.

10. The Table of the Periodic Law.—The table expressing the periodic law is most logically obtained, in the usual form of horizontal groups and vertical series, by letting the radius vector, passing from the center of the helix at E (see Fig. III*a*) through the inert gases, move in the direction of advance along the curve producing the table of the elements given on the following page. This table is perhaps the best arrangement of the elements possible on a plane surface.

It is most closely approached in the paper of Cuthbertson and Metcalfe, discussed on page 177. It is very useful for the presentation of some of the serial relations of the elements, but for the clear exhibition of many symmetries is greatly inferior to the helix, which has the advantage of three dimensions.

This is especially the case with regard to the odd and even series of Mendeléeff, which are approximated in his table with a certain unnatural naturalness, but are placed as far apart as possible on the helix, each pair, as potassium and copper, being at the opposite ends of a diameter. Their approximation in the Mendeléeff table is as when two points on the opposite sides of a hollow ball are brought together by the collapse of the ball. They are approximated because the respective heavy metal series *can* be monovalent, while in most respects they are the opposite of the light metal series. The copper-gold series stands as the antithesis—the "Spiegelbild"—of the alkali series. Copper and gold *can* be monads, but they are passing from a zero valence at the point of magnetic maximum and least compressibility and incipient dilatation, while the alkalies *must* be monads, and they hold a symmetrical position in relation to the opposite zero point in the area of greatest compressibility and beginning condensation. It is the same with the scandium series as compared with the gallium series.

The monovalency of the alkalies is grounded on the fact that they have one free electron to be given up, while the halogens are monovalent in that they are ready to take up one electron.

PERIODIC TABLE OF ATOMIC WEIGHTS.

E																	
Cn	H	Nu															Proto F
He	Li	Gl	B	C											N	O	F
Ne	Na	Mg	Al	Si											P	S	Cl
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
Kr	Rb	Sr	Y	Zr	Cb	Mo	. .	Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I
Xe	Cs	Ba	La	Ce	Pr	Nd	. .	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu	. . .
. .	. .	. .	. .	. .	Ta	W	. .	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	ABC
Ra Em	ThX	Ra	Io	Th	Ra-Ur	Ur											
O	I	II	III	IV	V III	VI II	VII I		VIII O		VII I	VI II	V III	IV	III	II	I

CHAPTER III.

General Relations of Symmetry.

Evidence of the naturalness and value of the helix is found in its use for the statement, comparison and discovery of complex relations among the elements as shown in Figs. IV, VII to IX and X to XII.

Many curious relationships, some homologies, some analogies, and some remote suggestions crowd these figures.

The main symmetry relations can be divided into four classes, though frequently several of these appear together as functions in one harmonic series. These classes are:

(*1*) *Longitudinal* relations, changing parallel with the axis of the figure.

(*2*) *Transverse* relations, changing at right angles to the backbone of the figure, and in this case they may be:

(*2a*) Symmetrical to the median vertical plane, and may be called *meridional* relations; or

(*2b*) Symmetrical to the horizontal plane, *equatorial* relations; or

(*2c*) Symmetrical to a plane placed 45° to the right of the vertical, and called *ecliptic* relations.

In many cases the change is fourfold, being controlled by both the meridional and equatorial planes, and may be called

(*2d*) *Quadrantal* relations.

Similar properties may be confined to the quadrants formed by the ecliptic and the vertical to the same, and may be called

(*2e*) *Ecliptic quadrantal* relations.

A group of allied, but unclassifiable relations are assembled on Fig. IX. They are associated in description with the group to which they are most nearly allied.

SECTION I.—RELATIONS WHICH ARE BOTH LONGITUDINAL AND TRANSVERSE.

1. Condensation and Expansion.

a. The Law of Transverse Condensation and Expansion.—This is the fundamental meridional relation. See Fig. IV.

In passing downward along each curve from an inert gas past an alkali there is a gradual condensation, as is indicated

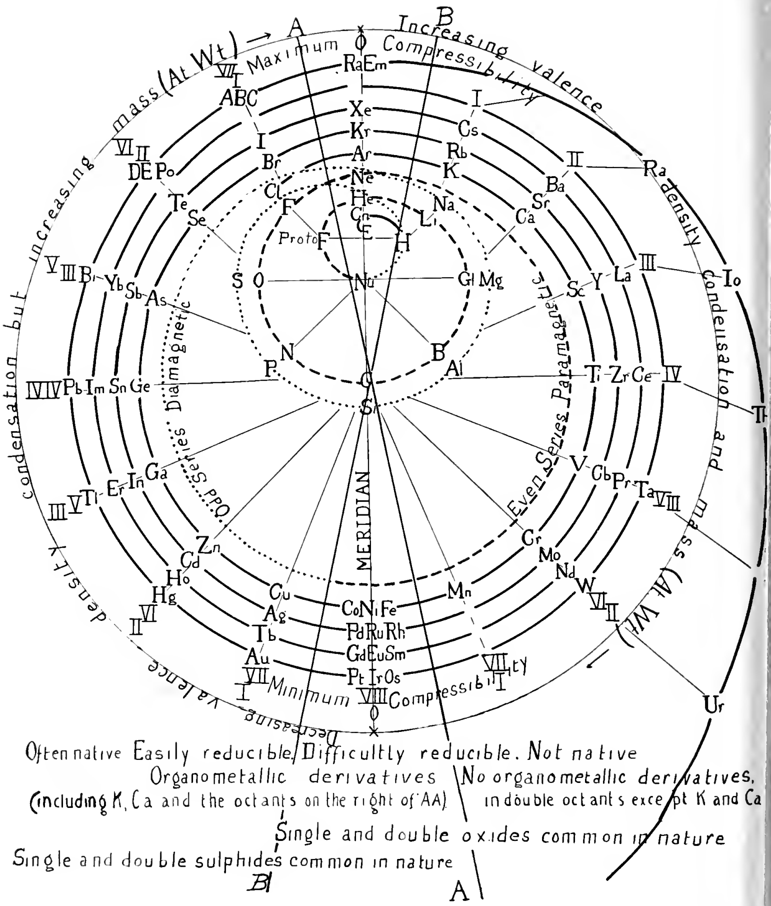

FIG. IV.—Meridional Relations. Part of these relations are strictly meridional; part divide on the line *A A* which passes *to the right of* C and Si; part divide on the line *B B*, which passes *between* C and Si. For condensation, see page 174; for magnetism, page 182.

by the increasing specific gravity and valence. In passing upward along the last half of the curve from a triad to a halogen there is a corresponding expansion, indicated by decreasing density and valence.

The potassium curve is in every way the central curve, and in passing down it the specific gravity increases regularly from near 1 at potassium to about 8 at iron, agreeing with the valence. In the ascending half of the circle there is a similar but less perfect agreement between the decreasing specific gravity and the valence or position number. A similar change occurs in the other circles. This is clearly expressed on the valence-volume graphs of Professor A. J. Hopkins,[1] who finds for each series the quotient

$$(valence)/(sp.\ gr.) \text{ or } (position\ no.)/(sp.\ gr.)$$

to be nearly a constant, and to be thus expressed by horizontal lines.

If we assume the molecules to be of the same size, there is then a twofold, threefold, and at last an eightfold condensation, which may be called the transverse condensation.

If the atom shows its greatest valence, all its attractive force is directed outwardly; if a lower valence, part of its energy is potentialized internally.

When the valence becomes thus multiplied and uncertain it is of little greater value than density in determining the "position" of an element in the series (see Chapter IV, p. 197).

We can realize how, with the addition of equal quantities of matter (equal groups of corpuscles), by a certain internal condensation, or self-condensation, elements may be formed with density and valence increasing from one to four or from one to eight. It is more difficult to conceive how, by the continued addition of matter of the same kind and in the same quantity, the curve should be continued by elements of regularly decreasing density and valence and that this alternation should be repeated rhythmically more than seven times. It may remotely suggest Tamman's[2] law in accordance with which the melting points of many compounds rise with increasing pressure to a

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[1] *Loc. cit.*, p. 160.

[2] G. Tamman: Krystallizieren und Schmelzen (1903), p. 184ff.

maximum and then, while the pressure continues to increase, sink gradually to a minimum.

b. The Law of Longitudinal Condensation: (*Density*)/(*Valence*) *or* (*Density*)/(*Position No.*) (Fig. I).—In addition to the transverse condensation there is also a longitudinal condensation. It is only in the central curve that valence and density agree from 1 in potassium to 8 in iron, so that $D/v = 1$.

The densities of the iron, rubidium, samarium, and platinum triads are as 8 : 12 : 16 : 22+, or D/v is as 1 : 1.5 : 2 : 3, and this, if we omit gases and poorly determined values, is true of each of the series of which the triads are a sample. Thus in the first or carbon octave we get, omitting oxygen and glucinum, which is always abnormal, an average value for D/v of 0.52; in the second or silicon octave, from sodium to phosphorus, 0.80. In the remaining circles, taking the right-hand or descending semicircle, we have (omitting two abnormal values) for the central or iron circle, 0.99, for the rubidium circle, 1.5, for the samarium circle, 1.92, and for the platinum circle, 2.9. These round up without forcing to

E	Nu	C	Si	Fe	Ru	Sa	Pt
(0)	$(^1/_3)$	$^1/_2$	$^2/_3$	1	$^3/_2$	2	3

This represents a gradual longitudinal condensation of each series, superimposed on the transverse condensation explained in the previous section. It is an interesting case under Goldschmidt's "Law of Complication."[1] This permits us to extrapolate the value 1/3 for the nebulium ring, representing the density of its elements in solid form, and zero for the origin E (see p. 161). These values are compared with other similar ones on page 197 and in Fig. I. This result may also be deduced from Hopkins's valence-density graphs.[2] It will be seen in these graphs that while the one containing potassium lies on the unit line, the first two lie above it, and the last four sink gradually below it, and in each case by distances which are proportional to the numbers deduced above.

In accordance with Goldschmidt's Law of Complication, the

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[1] Dr. Victor Goldschmidt: Ueber Harmonie und Complication, Berlin, 1901. W. H. Hobbs: Popular Astronomy, **146**, p. 345. Ann Arbor, 1907.

[2] *Loc. cit.*

Law of Longitudinal Condensation coincides not only with the law of the Octave in Music, but also with the fundamental law governing the order and frequency of the appearance of forms in crystals.

In Fig. II the model is made to sag in proportion to this increasing density to explain the gas area (see p. 187).

2. *Refractivity* (*Fig. VIII*).

a. The Longitudinal Element of Refractivity.—The valuable article of Cuthbertson and Metcalfe[1] on the refractivity of the volatile elements gives the following table for refractivities:

							H
							139
						He	
						72	
						144 × 1/2	
			N	O	F	Ne	
			297	270	192	137 × 1	
			P	S	Cl	Ar	
			1197	1101	768	568	
			299 × 4	275 × 4	192 × 4	142 × 4	
Zn	Ga	Ge	As	Se	Br	Kr	
2060			1550	1565	1125	850	
303 × 6			258 × 6	261 × 6	187 × 6	142 × 4	
Cd	In	Sn	Sb	Te	I	Xe	
2627			2675	2495	1920	1378	
267 × 10			267 × 10	249 × 10	192 × 10	138 × 10	
Hg							
1866							

My colleague, Professor A. L. Kimball, has been so kind as to calculate for me the refractivities of other elements expressed in the same form, $(u - 1)\ 10^6$, and when these are all plotted on the helix the number for hydrogen comes below that for helium and then the series of factors expressing the longitudinal refractivity is complete as follows:

$^1/_4$(?) $^1/_2$ 1 4 6 10

This extends the law to the outer half of the alkali series.

This regular and common increase of refractive power in passing longitudinally along each of the series, as the halogens

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[1] Phil. Trans., A, **207**, 135 (1907).

or inert gases, is extremely interesting, as it finds expression after swinging hydrogen into its place with the alkalies.

Dividing the above row of factors by four to make it comparable with the row expressing the longitudinal compression, we have:

Coefficients of compression	($^1/_3$)	$^1/_2$	$^2/_3$	1	1 $^1/_2$	2	3
Coefficients of refractivity	($^1/_{16}$?)	$^1/_8$	$^1/_4$	1	1 $^1/_2$	2 $^1/_2$	

The similarity of the two series is striking, and can be carried one term farther than appears in the rounded out values, since 2 of the compression series is equal to 2.2 by taking the most favorable values, and 2.5 of the other becomes 2.42 in the same way.

I have permitted myself to extrapolate a possible refractivity, 36, for coronium, which occupies the top of the first circle.

b. The Transverse Element of Refractivity (*Fig. VIII*).—An inspection of the figure shows, in addition to the great longitudinal increase in refractivity, a more moderate transverse variation.

Within the limits of normal refraction the common factor increases either way from a minimum, 140, in the inert gases.

This normal refractivity prevails in the upper three-fourths of the low-fusing semicircle, while the area of colored ions lies just opposite to it in the lower three-fourths of the high-fusing semicircle.

It is thus an ecliptic function and is so treated on page 195 and in Fig. VIII. In the region of expansion, transparency and refraction prevail. In the region of condensation, opacity, absorption and therefore colored ions prevail.

3. Vibration Period(?) (*Fig. I*).

Batschinski[1] has attempted to show that the period of vibration of the elements varies as the square root of the atomic weights. Assuming that the vibrations of the corresponding atoms in the different series must be in some simple and harmonic relation to each other, he suggested as the simplest formula for the period of vibration:

$$T = \pi\sqrt{\frac{m}{g}}$$

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[1] A. J. Batschinski: Z. physik. Chem., **43**, 372 (1893).

where m is the mass of an atom, or the atomic weight; g is a constant force-coefficient.

Thus the period of vibration (T) varies as the square root of the atomic weight m. To explain what he means by "vibration" Batschinski states that this formula is based on the assumption that "a frictionless atom is subjected to an attractive force which is the same for all atoms and changes in proportion to its distance from a center."

Curiously, Sutherland has obtained the same ratios independently for the alkalies and alkaline earths, and in part for other series, by the formula

$$p = \left(\frac{M}{d}\right)^{\frac{1}{3}} \frac{(M)^{\frac{1}{3}}}{\sqrt{T}}$$

where M is the mass, T the melting point, d the density.[1]

Batschinski arranged the roots in the order of the elements in Mendeléeff's table, and found that for a part of each series the numbers could be factored into a constant multiplied into the digits 1, 2, 3, 4.

He took this harmonic relation to be the expression of the relative vibration periods of the elements.

Without accepting this conclusion it is interesting to see how much more symmetrical the table becomes when the roots are arranged in our proposed periodic table, and factored so that the numbers in the horizontal column containing potassium become 3, as this expresses the ratio most simply, as given in the table below.

The longitudinal factor increases with remarkable regularity in the simplest arithmetical progression.

In the transverse direction along the line of the helix curve, there is a slow and somewhat regular increase in the constant factor which is, of course, an average, but one of quite closely agreeing numbers.

The controlling function in both the equations cited above is M, or the atomic weight; and it is clear that the table is only another form of expression for the harmonic relations of the atomic weights.

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[1] W. Sutherland: New Periodic Property of the Elements. Phil. Mag., [5] **30**, 318.

TABLE OF THE SQUARE ROOTS OF THE ATOMIC WEIGHTS FACTORED INTO A CONSTANT (WHICH IS PLACED BELOW) AND THE SERIES OF NUMBERS IN SIMPLE ARITHMETICAL PROGRESSION.

E																		
Cn	H	Nu															Proto F	
He	Li	Gl	B	C											N	O	F	
1	1	1¼	1½	1½											1½	1½	1½	
Ne	Na	Mg	Al	Si											P	S	Cl	
2	2	2	2	2											2	2	2	
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
Kr	Rb	Sr	Y	Zr	Cb	Mo	..	Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I	
4	4	4	4	4	4	4	..	4	4	4	4	4	4	4	4	4	4	
Xe	Cs	Ba	La	Ce	Pr	Nd	..	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	..	..	
5	5	5	5	5	5	5	..	5	5	5	5	5	5	5	5			
..	..	..	..	..	Ta	W	..	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		
					6	6		6	6	6	6	6	6	6	6			
Ra Em	..	Ra	Io	Th	Ac	Ur												
7		7		7		7												
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
212	213	226	231	237	232	239	247	244	249	247	250	258	264	275	264	275	292	Constant

It seemed worth while to print it as an additional indication of the naturalness of the order of elements upon the helix, and illustration of the usefulness of the proposed table for the presentation of such relations.

4. Specific Volumes.

Professor Hopkins's graph of specific volume[1] is reproduced in Fig. I, and continued in a dotted line to express the probable relations of the two possible alkalies beyond caesium.

This presents, as Professor Hopkins has shown, the essential relation of the atomic-volume graph of Meyer, given on Fig. I. The latter shows the relation of atomic weight divided by density to atomic weight; the former shows the relation of specific volume or 1/(*density*) to the atomic weight.

Professor Hopkins has shown that in plotting (as is done in Meyer's graph) the atomic weights on the axis of ordinates and the value (*atomic weight*)/(*density*), or (*atomic weight*) × 1/(*density*), on the axis of abscissas, the atomic weight appears actually as a factor in both axes, and produces the same effect as if the axis of abscissas ran upward at an angle of 45°, and the values of the specific volumes (or 1/*density*) were plotted with these axes. This explains why in the atomic-volume graph of Meyer the apices of the two first curves at the alkalies lithium and sodium slant upward at a high angle, and those of the remaining ones run upward on a higher but parallel slope. In the specific-volume graph these points are on nearly parallel and horizontal lines, agreeing with the curves of the helix.

SECTION II.—THE MERIDIONAL RELATIONS (SEE FIG. IV, p. 175).

The vertical median plane passing through the zero points is of primary importance. It separates all those values which depend upon the fact that each curve passes from the zero point downward with increasing condensation to a maximum in the triads, and then rises with decreasing density to the zero point and place of sudden change. This conditions density, valence, and those regularly increasing relations

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[1] *Loc. cit.*, p. 160.

which are not reversed or confused by the greater density of the lower semicircle.

1. The Odd and Even Series of Mendeléeff—Magnetism.—The elements to the right of the median plane upon the five larger circles and upon the whole first or carbon octave circle form the even groups of Mendeléeff. As determined by Carnalley, these elements are for the most part paramagnetic (except zirconium). The elements to the left on the four large circles and upon the whole of the second or silicon circle and hydrogen form the odd groups of Mendeléeff. They are diamagnetic. It is remarkable with what fidelity this relation is expressed by the two curious curves in Fig. IV, which start with nebulium; one passes through hydrogen and the silicon circle and continues beneath the left-hand half of the four large circles to indicate that they all are odd and diamagnetic, while the second curve is the exact counterpart of the first in position and meaning. They cut each other in helium and neon, thus indicating that the inert gases are nonmagnetic and in an odd-even series.

2. Organometallic Compounds.—The elements of the half-octave, the octaves and on to calcium on the first double octave form organometallic compounds; then for the remainder of the elements those on the left of the line *A A* in Fig. IV do the same, while those on the right do not enter into organic compounds.[1]

The law is a direct function of the law of condensation described above.

Passing longitudinally along the helix the condensation does not become so great as to inhibit the formation of organic compounds until the first double octave is reached. Then the transverse condensation comes into play and thenceforward, where it reinforces the increasing longitudinal condensation, there are no organic compounds.

As we go down the first double octave the increasing transverse condensation prevents the formation of organic compounds, after calcium is passed, until the iron group is reached;

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[1] I am indebted to Dr. Charles A. Rouiller for the accurate statement of this rule.

thereafter the increasing dilatation along the upward branch of the curve permits their formation, and this rule holds for the rest of the helix.

3. Natural Oxides and Sulphides.—Single and double oxides are most common for the elements on the right-hand downward curves of condensation, single and double sulphides for those on the left-hand upward curve of dilatation. Of elements on the meridian, those in the middle form both, those at the ends neither. See Fig. IV.

4. Reducibility, Native Occurrence.—If a line *B B* (Fig. IV) be drawn just to the right of the meridian and passing through the center so as to leave carbon on the left and silicon on the right, those on the right side are of difficult reducibility, those on the left are easily reduced.

The easily reducible elements on the left naturally often occur native. Those on the right rarely occur native. Platinum is an exception.

5. Atomic Volumes and the Completion of the Atomic Volume Diagram (see Figs. I and V).—Lothar Meyer's diagram of atomic volumes is reproduced upon Fig. I.

It has been prolonged as suggested by Benedict,[1] and carried back to its origin in accordance with the calculations given below. A break has been left in it at a point where there are no recorded observations for a probable upward bend at the place of the next alkali beyond caesium.

This diagram is formed by plotting the atomic volumes (obtained by dividing the atomic weight by the density) as ordinates, and the atomic weights as abscissas. It expresses mainly a transverse function, and in the longitudinal direction distinguishes only the long and the short groups, the double octaves and the octaves.

This is shown clearly by the accompanying table (p. 185), which is formed of the quotients obtained by dividing the atomic volume of each element by the atomic volume of the element immediately above it in the same series, as given in Meyer's table. Thus the atomic volume of sodium divided by that of lithium is equal to 2, and so on.

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[1] Z. anorg. Chem., **3**, 40.

Since the elements from rhodium to antimony have practically the same atomic volumes as those in the lower row from osmium to bismuth, I have assumed that the intervening unknown atomic volumes would also be the same.

It is interesting that these ratio numbers range closely about unity in the double octaves, showing that there is no longitudinal variation within these four circles.

They grade from 1 to 2 in passing from the double octaves to the octaves, and range about two in the octaves, with a distinct maximum at the bottom of the curve at carbon.

It is therefore possible to extrapolate quotients for the elements in the half-octave, as is done in the table (numbers in brackets). An inspection of the table will show that as the quotient under chlorine is 1.1 and that under fluorine is 2, that under protofluorine may be assumed to be 3.

From this ratio number the atomic volume of protofluorine can be calculated as follows:

$$\frac{At.\ vol.\ of\ F}{At.\ vol.\ of\ Proto\ F} = 3.$$

$$At.\ vol.\ of\ Proto\ F = \frac{At.\ vol.\ of\ F}{3} = \frac{13}{3} = 4^1/_3.$$

In the same way the probable atomic volumes of hydrogen and nebulium are calculated and the three numbers are placed against their respective elements. A more forced extrapolation is entered on the table for the atomic volumes of the inert gases by taking the atomic volume of neon to be proportionate to those of magnesium and sodium and the quotients above the inert gases proportionate, respectively, to those on the right. From the atomic volume of neon these quotients give the atomic volume of the other inert gases. This result has a value not for the exact numbers which are obtained but to show the great probability that these values are higher than those of the adjacent alkalies and that the culminations of the curves in Meyer's diagram are at the inert gases and not at the alkalies.

With these numbers the atomic volume curve in Fig. V has been drawn.

The right-hand loop is identical with the Meyer diagram

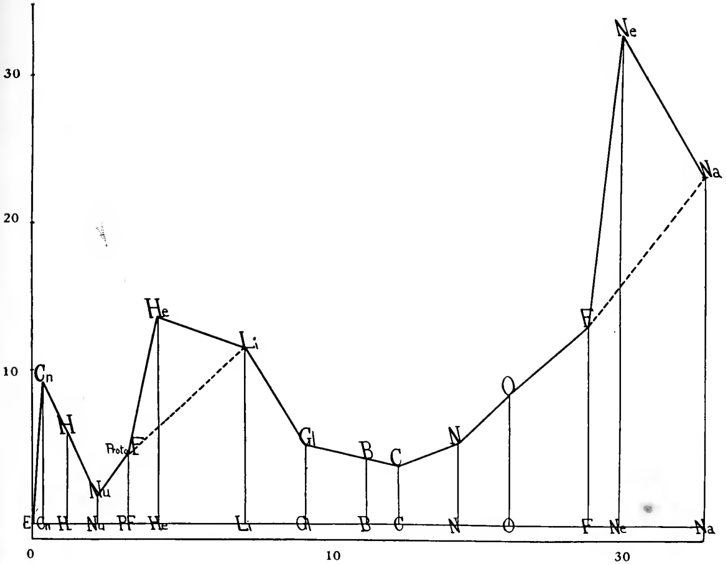

FIG. V.—The atomic-volume curve continued back to the origin and drawn with its culminations in the inert gases. The Li-Na curve continued along the dotted line is the first loop of Meyer's curve. The other parts are calculated from the data given on page 183.

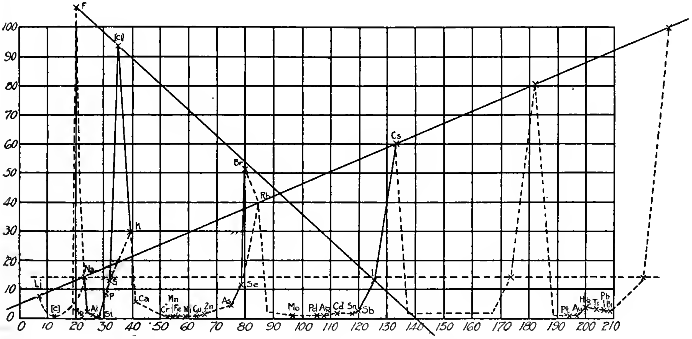

FIG. VI.—The atomic weight-compressibility curve of T. W. Richards altered to show the possible position of the halogens in solid form and to extrapolate alkalis beyond caesium (see page 186).

The line Br-Cl shows the probable great compressibility of fluorine in gaseous form and an impossible negative compressibility of halogens beyond iodine. The horizontal line of heavy dashes passing through I shows the probable position of the halogens (if they could be measured in solid form) below their present one on the chart.

ATOMIC VOLUME QUOTIENTS.

Cn(13)	H(5.7)	Nu (1.3)														Proto F (4.3)	
(1.5)	(2.1)	(3.8)															(3)
He(19)	Li	Gl	B	C											N	O	F
(1.7)	2	2.8	2.7		3.2										2.7	2	2
Ne(33)	Na 23.7	Mg 13.9	Al	Si											P	S	Cl
(2)	1.9	1.8	1.6	1.1											1	1.1	1.1
Ar(66)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
(1.2)	1.2	1.3	1.5	1.2	1.3	1.3		1.2	1.2	1.3	1.4	1.4	1.3		1.4	1.2	1.1
Kr(78)	Rb	Sr	Y	Zr	Cb	Mo		Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I
(1.5)	1.3	1	1	1				1	1	1	1	1	1.1	1.1	1.2		
Xe(116)	Cs	Ba	La	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb		
				1				1	1	1	1	1	1.1	1.1	1.2		
					Ta	W		Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	ABC
						1.3											
Ra Em		Ra	Io	Th	Ac	Ur											

if we follow down the dotted line from sodium. The newly calculated lithium-hydrogen loop is exactly symmetrical with this. The calculated value 13 is given to coronium and it finds its place as a final culmination in harmony with the preceding culminations of the inert gases and from coronium the line goes down to the origin at the ether.

The atomic-volume curve of Meyer, which omitted the inert gases, had its culminations in the alkalies. The above construction shows that these culminations are most probably in the inert gases. This would signify that the atomic volumes of the inert gases, if obtained in terms comparable with those of the other elements, would be much greater than those of the alkalies and thus the density much less. This makes the atomic-volume diagram harmonize exactly with the helix and gives a considerable value to the numbers used above.

We may further calculate the possible density of the three elements in the solid form, since, if $(at.\ vol.) = (at.\ wt.)/(density)$, then $d = (at.\ wt.)/(at.\ vol.)$. We obtain for coronium $d = 0.3/13 = 0.023$, for hydrogen $d = 1/5.7 = 0.16$, for nebulium $d = 2/1.3 = 1.5$, for protofluorine $d = 0.7$.

This makes the densities of the half-octant agree with those of the other circles in increasing downward to a maximum.

6. *Compressibility* (*Figs. IV and VI*).—The compressibility curve of Professor Richards,[1] in large part, agrees closely with the helix and in part diverges from it strongly. A very simple and probable assumption concerning chlorine and bromine would bring it into exact accordance with the helix, *viz.*, that their compressibility *in solid form* would be much less than that given in the table. To show the plausibility of this assumption I have drawn a line through chlorine, bromine, and iodine on the figure, and obtained therefrom an exaggerated compressibility for fluorine (which I have drawn on the figure with dashes longer than those used on the original) and an impossible negative compressibility for possible halogens beyond iodine.

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[1] The Compressibility of the Elements and Their Periodic Relations. T. W. Richards: Pub. Carnegie Inst., 1907.

I have then drawn a second nearly horizontal line (in long dashes) through iodine to fix the probable position of the other halogens in solid form. As iodine is far below caesium we may believe bromine would be far below rhodium, chlorine far below potassium, fluorine below sodium, and protofluorine below lithium.

This harmonizes perfectly with the position of the line of the halogens in Fig. IX parallel with the vertical diameter, near to and equidistant from the line of least compression.

I have therefore drawn a dotted line from potassium to a point just above sulphur at the new position of chlorine to complete the second loop, and from rubidium to the new position of bromine, just above selenium, to complete the third loop. I have then drawn a third line through the alkalies and extrapolated two alkalies beyond caesium, and placed the emended graph upon Fig. I.

7. *The Gas Area* (*Figs. II and IX*).—As exhibiting a maximum of volatility, the gases occupy an irregular area in the center of the low-fusing semicircle. It is very peculiar that, as indicated by the chain in Fig. II, the area is symmetrical to the equator in the double octaves and to the ecliptic in the octaves.

The laws of condensation described in Section I explain the area of the helix within which the elements are gaseous at normal temperature. The hydrogen circle contains elements of so small density that they are permanent gases. In the second circle the passage from helium to lithium involves sufficient condensation to compel the solid nonvolatile condition which continues through carbon. Turning upward on the curve, the dilatation is sufficient to immediately cause the change to gas at nitrogen. This continues upward through that half-circle, but passing the zero point at neon, the curve sinks into the solid series immediately below the gas area, and continues in the region of solid elements to silicon. Turning upwards from silicon, the gas boundary is seen to just graze the highly volatile elements phosphorus and sulphur, and to just cut through the liquid bromine in a very significant way.

We may compare the helix to a slanting log sunk into the water. The first coil, containing hydrogen, passes around the log without touching the water and is wholly gaseous. The second passes into the water between helium and lithium, and becomes solid but quickly emerges on the other side beyond nitrogen, and is gaseous during most of the circuit. The next downward turn passes quickly into the water at sodium, and is under the surface through three-quarters of the turn. The succeeding turns emerge only far enough to make place for a single gas, and not far beyond the radium emanation we may believe that the whole circuit would be solid if conditions favored its formation.

If the reason for the formation of gases on the upper side of each curve is found in the law of transverse condensation, the reason for the diminution of the gas area in passing from curve to curve in the direction of motion is due to the law of longitudinal condensation. In Fig. II I have indicated this by the slanting position of the helix which dips to the right at such an angle that the line of boundary of the gas area (represented by a chain) passes across it horizontally like a contour line. Above it is drawn the graph expressing the law of longitudinal compression and of increasing density and the model is so placed as to make the chain horizontal to symbolize the amount of depression due to this increased density.

It is very curious and interesting, however, that while this contour relation holds with regard to the large curves and the gas boundary is parallel here to the equator of the figure, in the small circles this boundary sinks with an angle of 45° and places itself parallel to the ecliptic of fusion, (See Fig. VIII) bounding the volatile semicircle. Thus the gas area sags to include the two gases oxygen and nitrogen, which are found to be abnormal also in their density (see page 201) and in their atomic heat, as shown in the section below.

8. The Rock Area.—In Fig. IX the apex of the gas area which enfolds the elements of the nebulae and the elements of life tapers upward and forward like a flame, forming the center of the volatile semicircle. A similar figure, pointing downwards and backwards, forms the center of the high fusing semicircle and includes the rock-making elements, silicon, aluminium, magnesium, sodium, potassium, calcium and iron. This forms the lithosphere and points downward and backward toward the centrospere, where are the heavy magnetic triads.

Inspect this figure and see how suggestive is the position of every element in the little group.

Potassium stands at its apex, suggesting the lightest feldspar and the lightest of the rocks, as pegmatite.

Next below is sodium and beside it and a little below is calcium, suggesting the soda-lime feldspars, the intermediate rocks and the Howardites among the meteorites. Thus far we are in the salic region.

Far below is magnesium, suggesting the heavy olivine, the ultrabasic rocks and the Chondrites among the meteorites.

Much farther below are iron, cobalt, nickel, suggesting the sesquioxide segregations, the basic border-rocks, and the Pallasites and Siderites among the meteorites. This is the femic region.

On one side of the middle of this row of low-valence bases the single trivalent base aluminium links the whole with the single tetravalent acid-maker silicon at the center.

9. *The Stability of the Oxides.*—When subjected to rising temperatures the stability of the oxides of the elements varies according to two laws:

(*a*) When the elements are followed radially the stability decreases inwardly (as from caesium to lithium) in the first semicircle, and decreases outwardly (as from fluorine to iodine) in the second semicircle.

(*b*) When they are followed along the line of the helix (as from potassium to titanium) the stability decreases through the first semicircle (as rubidium to molybdenum), increases through the third octant (as copper to germanium) and decreases through the fourth octant.[1] Compare electropotential relations (p. 190).

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[1] A. E. Garrett: The Periodic Law (1909), p. 193.

SECTION III.—EQUATORIAL RELATIONS (SEE FIG. VII).

The diametral plane is prepotent, and where the relations are also strongly influenced by the equator they are mostly divided in quadrants. The main equatorial contrast is that the upper half of the double octaves is strictly homologous with the whole of the single octaves, and shares with them the simple valence, the marked changes at the zero point, and the marked contrast on either side of it. The lower half of the double octaves has complex valence, and culminates without strong contrasts in the triads, in the midst of the heavy, highly-colored, and magnetic metals. Above, along the axis, in a region of ideal expansion, are strung the inert gases, without elective affinity or allotropic forms—strict unitarians. Below, in a region of greatest compression and narrowness, are strung the four triad groups, with valence ranging from one to eight—true trinitarians, the varying valence symbolic of sectarian tendency.

The equator thus divides the whole into a northern hemisphere of maximum compressibility having elasticity, high electropotential, and all the elements of elevation, evolution, and civilization, and a southern hemisphere of minimum compressibility, comparatively inert and undifferentiated, containing the heavy metals and the most complex molecules. The upper hemisphere is in the region of simplest spectra, the lower in that of the most complex spectra, and in many series the lines at the blue end of the spectrum appear in the elements at the top, and there is a gradual passage downward toward the red end of the spectrum.

SECTION IV.—THE QUADRANTAL RELATIONS.

1. Electropotential Relations (*Fig. VII*).—Abegg's table[1] of the electropotentials finds very clear expression upon the diagram by decreasing plus and minus signs. It is in general a quadrantal arrangement. The strong electropositive capacity of the alkalies decreases regularly to zero, at the bottom of the first quadrant. The strong electronegative capacity of the halogens decreases regularly to zero at the bottom of the fourth quadrant. Here at the equator the sign changes, and

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[1] Z. anorg. Chem., **39**, 330 (1904).

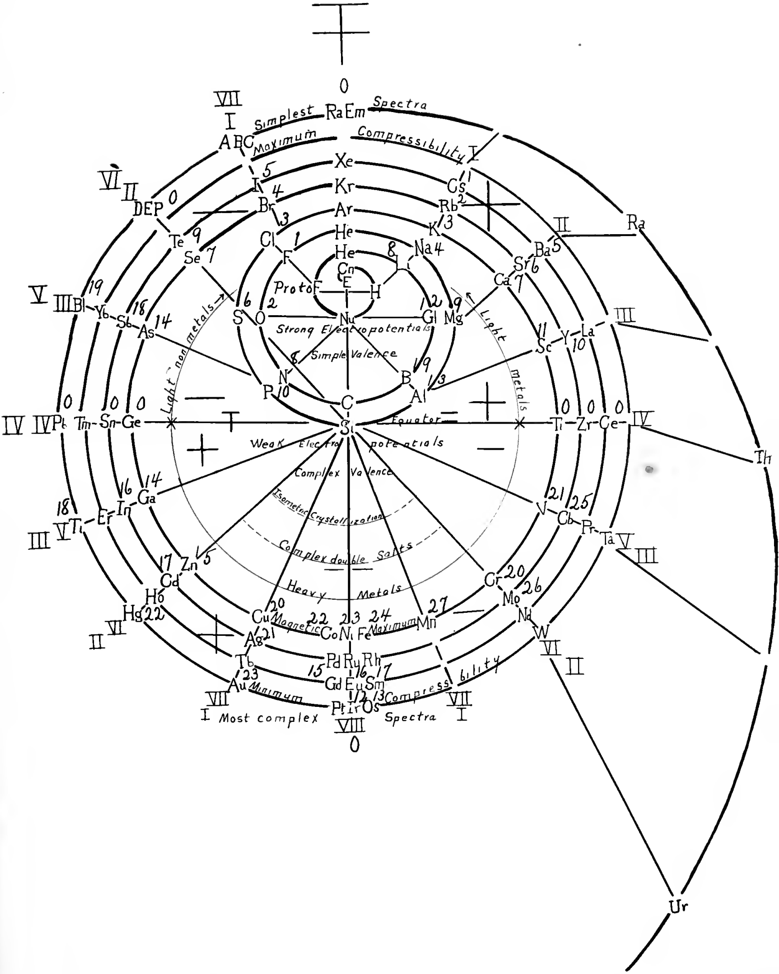

FIG. VII.—Equatorial and Quadrantal Relations. Values of the Electropotentials of the Elements in Detail. The printed numbers represent the order of these values, beginning with the highest. The written numbers give the group or longitudinal atomic weight differences. See page 190.

the value becomes plus in the third quadrant and minus again in the second, but in each case with lessened power, the electronegative force decreasing to a minimum near molybdenum, the electropositive to a minimum between mercury and silver.

The details of this relation are also brought out clearly by the numbers placed against the different elements. A curious contrast is brought out, in that the electronegative capacity decreases in the direction of the axis of the helix, while the electropositive capacity decreases in the reverse direction. The negative decrease goes outward along the halogen series regularly, but springs back to take in oxygen. It then starts along the oxygen series regularly but springs back to take in nitrogen. It then starts along the phosphorus-arsenic series regularly, but springs back to platinum, iridium, osmium and arsenic, and thenceforward there is no regularity.

The positive decrease, on the other hand, starts with caesium and goes regularly backward to sodium. It then starts back to take in the barium series before taking in the rest of the alkali row, and so on. This is similar to the order of stability of the oxides (p. 189).

This finds a possible explanation in that the relation is a function of the condensation. The electronegative force *decreases* along each horizontal series (as the halogens) with increasing longitudinal condensation, and decreases down each circle with increasing transverse condensation. The electropositive force *increases* along each horizontal series (as the alkalies) with increasing longitudinal condensation. It is a question in each case whether the longitudinal or transverse condensation shall be the more effective.

The electronegative maximum is at fluorine at the point of least condensation. The line down to oxygen is a direction of increasing transverse condensation, and the line along the halogens is a direction of increasing longitudinal condensation. The former prevails; oxygen comes in second, and then the effective increment of condensation follows along the halogens and the sulphur series, but before tellurium is reached the transverse increment of condensation raises nitrogen to a condensation greater than tellurium, and so nitrogen precedes tellurium.

After phosphorus, the next value jumps to the most condensed portion of the opposite quadrant—the platinum group—and then oscillates between these quadrants with a curious rhythm to end near molybdenum.

The plus series is the counterpart of the minus one, beginning at the most condensed end of the alkali group and working backward to lithium. The curious torsional arrangement of these potentials suggests a connection with the dia- and paramagnetic relation.

It is even more difficult to understand the passage from the electronegative halogen line through the inert gases to the electropositive alkali line. It is symbolized rather than made intelligible by the statement that it is a passing through zero with change of sign.

This may find its physical explanation in the idea that on each ascending arc the maximum of dilatation is reached or approached at the line of the inert gases, and this is also near the maximum of mobility and has minimum valence. Here the addition of the smallest mass equal to about a hydrogen atom—the equivalent of a single interspace or interweight—to each halogen (see Fig. X and Sec. 5, p. 202) brings about an exceptional equilibrium in the corresponding inert gas, wherein there are no free electrons, and a condition like that of a haloid compoundis reached, and this is so stable that it requires the addition of the maximum mass, equal to a helium atom or more, to break the "dead center" as we say in mechanics, or to pass the zero point as we say in mathematics, and give rise to an atom of such great mobility that a complete rearrangement of the rings occur sand an atom with one free electron and a maximum positive electropotential capacity is formed in place of one lacking one electron and with the greatest electronegative character.

It is, however, to be noted that at first in the octave the minimum density is reached at the culmination in the inert gases; in the double octaves, beyond the culmination at the alkali line. See Fig. XI.

It is further interesting that each halogen approaches the zero point with a less electronegative capacity than its predecessor and emerges as an alkali with a greater electropositive capacity than its predecessor.

In comparing the inert gas with a halogen compound, I have followed an unpublished suggestion of my former pupil and good friend, Professor C. S. Palmer, who has done so much to increase our knowledge of the periodic law, that the inert gases are inert, not because they are without chemical affinity, but because they in a sense combine the electropositive and electronegative character, and so I have put ± above them, with the large size appropriate to this position.

2. *Melting Points of the Haloids.*—The mean melting-point curves of the normal chlorides, bromides, and iodides of the elements[1] take the same quadrantal arrangement as the electrical potential.

From a maximum in the alkalies the melting point decreases in the octaves and rises again to the halogens. In the double octaves the decrease in the first quadrant is followed by an increase in the second to a subordinate maximum in the copper series, followed in its turn by a decrease in the third quadrant, and a sharp increase to the halogens in the fourth.

The graph is reproduced on Fig. I. The dotted line is introduced only to connect the significant parts of the same.

3. *The Shifting of the Colors of the Spectra.*—The elements of the different subgroups or radial series, as the alkalies, have spectra which are similar in the number of bright lines visible and the groups into which those lines may be divided.

Their characteristic or homologous lines change regularly in color, in passing outwardly in radial direction, and this change is toward the red end of the spectrum in the first and third quadrants, and toward the violet end, so far as observed, in the second and fourth quadrants.[2]

4. *Crystallography* (*Fig. VII*).—The ecliptic and its vertical divides the helix into a lower, upper, and two lateral quadrants. In the lower quadrant the cubic system prevails,

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[1] Carnelley: The Periodic Law. Chem. News, **53**, 171.

[2] A. E. Garrett: The Periodic Law (1909), p. 171.

though some few elements show also the analogous rhombohedral system.

In the two lateral quadrants the tetragonal, rhombic and monoclinic systems prevail. Indium is cubic, and vanadium, magnesium, bismuth and antimony are hexagonal, generally as an allotropic form.

In the upper quadrant only the alkalies are known in crystal form and then are quadratic, except lithium, which is cubic. There is thus the greatest symmetry connected with the greatest condensation.

5. The Law of Dulong and Petit (*Fig. IX*).—The failure of the elements to obey the law of common atomic heat stands in distinct relation to the tendency to form gases, but the area containing the abnormal elements is almost symmetrical to the meridian. It coincides with the upper part of the gas area, and the right-hand boundary of the latter is continued downward to include glucinum, beryllium, carbon, silicon, phosphorus and sulphur when it joins again the left-hand boundary of the gas area. It requires thus a little greater condensation to establish the law of common atomic heat than to introduce the solid form.

SECTION V.—THE ECLIPTIC RELATIONS (FIG. VIII).

1. Fusibility and Volatility.—A diameter bisects the first and third quadrants like an ecliptic, having on one side the high-fusing metals and on the other the volatile and low-fusing elements. The maximum fusing point lies between manganese and chromium, and the high-fusing area extends to the beginning of volatility in the zinc series. Thus this diameter has, curiously, the liquid mercury at one end and the luminous radium at the other. It is further remarkable that this diameter of the large circle cuts off a sectant from the small circle which separates the three high-fusing element groups from the five low-fusing, volatile or gaseous groups. This is slightly misleading, since in a true figure the small (octant) circle is raised above the fusion diameter. This sector dividing the small circle remains, however, strictly parallel to the fusion diameter when the figure is correctly drawn (see Fig. III), so

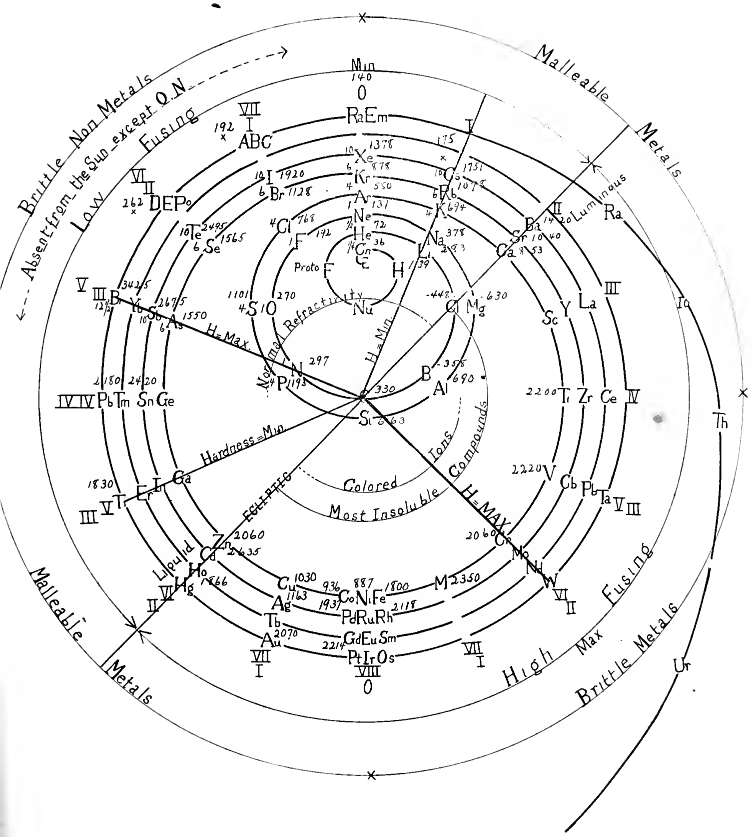

Fig. VIII.—Ecliptic Relations. Refractivity in Detail.

The large number on the right is the coefficient of refractivity. The small one at the left represents the factor to be multiplied into the constant at the border to obtain this refractivity.

For refractivity see page 177; for colored ions, page 195; for malleability, page 196; for insoluble compounds, page 195; for fusibility, page 194; for hardness, page 196.

that the suggested symmetry is not impaired. It was by pure chance that the figure was drawn so as to make these two lines coincide.

2. Solubility.—The ecliptic also separates the elements forming mostly insoluble compounds, on the lower or heavy side, from those forming mostly soluble compounds, on the upper volatile side (Carnelley).

3. Elements Wanting in the Sun.—Most peculiar of all the ecliptic relations is that the middle quadrant of the volatile semicircle contains elements which are wanting in the sun, except oxygen and nitrogen, the atmospheric elements, in the center. Have they been volatilized therefrom, or is it only a defect of spectrum analysis?

4. Colored Ions.—The lower three-quarters of the high-fusing semicircle are occupied by the colored-ion makers, and this is essentially an ecliptic relation, though this relation is first established an interspace below the light malleable metals.[1]

5. Refractivity.—The upper three-quarters of the low-fusing semicircle are occupied by the transparent refrangible elements which also obey the law of longitudinal periodicity, as described in Section IV, 2, p. 177.

That this area is the "Spiegelbild" of the colored-ion area is significant, since the transparency of the volatile elements which make refraction possible is the opposite, as a color producer, of the strong absorption of the colored metals, and the two exclude each other.

As the elements obey the law of the octave in their refractive capacity in the region of greatest dilatation, so in the region of greatest condensation, absorption takes the place of refraction and colored ions are produced.

The line representing the distribution of colored ions is dotted at either end to cover the transitional elements which produce partly colored ions and partly uncolored ones. This line divides the elements exactly except that thallium and bismuth sometimes produce colored ions. After the above result was worked out the diagram—the arbitrary diagram he calls it—of Rudorf[2] was found.

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[1] Carey Lea: Chem. News, **73**, 203 (1896).

[2] George Rudorf: Periodic Classification (1900), p. 119.

A comparison shows the greater elegance of the above arrangement, especially in bringing out the relation of colored ions to refractivity.

6. Hardness (*Fig. VIII*).—The hardness of the elements is distributed as a peculiar variant of the ecliptic relation.

Platting the table of Von Rydburg,[1] the maximum hardness 10 comes at the ideal center in carbon. The line of maximum hardness is the radius through chromium at right angles to the ecliptic.

At the center this line branches symmetrically and two minima pass along the radii through gallium and lithium, and a subordinate maximum, instead of going straight on through selenium, passes one point to the left through arsenic. To avoid confusion this is shown on the diagram by lines and not by introducing the numbers. Only the averages are indicated by the relative size of the type.

The law is very clearly realized and this illustrates a useful method of expressing a complex relation by means of the helix.

7. Valence.—Valence is a purely transverse function; that is, in passing along the alkalies the valence cannot be said to change in any way from unity; and so in the other groups.

The principal valence is a purely meridional function, increasing from O at the top to VIII at the bottom of the meridian either way.

The whole valence has an ecliptic quadrantal relation. It is simply O to IV in the first quadrants; complex O to IV and VIII to IV in the third. In the second and fourth quadrants it is IV to O and IV to VIII.

This is best shown on Fig. III.

8. Ductility (*Fig. VIII*).—The meridian and equator divide the helix into quadrants symmetrical to the ecliptic. The first and third quadrants contain the malleable metals, the second contains the brittle metals, and the opposite fourth quadrant contains the brittle nonmetals.

9. The Quadrilateral of Life (*Fig. IX*).—At the base of the gas area is a strong quadrilateral, CHON, a symbol used many

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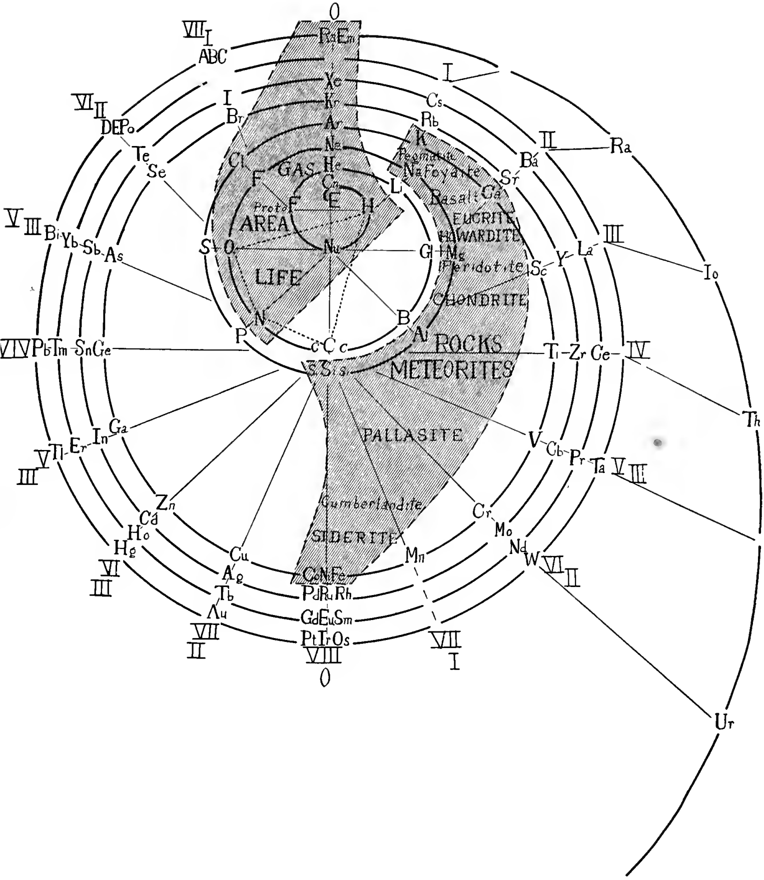
[1] Landolt-Börnstein: Physikalisch-Chemische Tabellen, 1905.



IG. IX.—Allied relations of partial or complex symmetry which do not come into the preceding categories. They are described in the section with which they are most nearly related: The gas and rock areas as diametral on page 187; the law of Dulong and Petit as equatorial on page 194; and the quadrilateral of life as ecliptic on page 196.

years ago by the fine zoologist, Henry James-Clark, to signify the life-bearing elements, or protoplasm. Of this quadrilateral ON represents the atmosphere, OH the ocean, OC carbonic acid and CH the hydrocarbons; while the quadrilateral is fringed by all the subordinate elements of protoplasm, and has Na and Cl, the characteristic compound of the salt water, the common menstruum[1] of life, in a most symmetrical position directly above.

SECTION VII.—THE LAW OF THE OCTAVE.

In a sense the law of the octave holds not only transversely but longitudinally. We have already expounded and expanded Newland's law of the octave, as it applies to the elements transversely (Chapter II, p. 170). Each inert gas is the first note in a new octave, each alkali the second—the half-octave is followed by two octaves, by four double octaves and one quadruple octave.

Proceeding in the other direction, or longitudinally, and going out from the center in each series, as the alkalies, the elements, barring in some cases polymerization and the gaseous condition, have been found to increase in density according to Goldschmidt's law of complication, which is also the law of the harmony of the octave in music. Many other harmonic relations which depend more or less upon the density follow in varying degree the same law, as shown in the following table:

Goldschmidt's Law	0	1/3	1/2	2/3	1	3/2	2	3		∞
Condensation (see p. 174)	0	1/3	1/2	2/3	1	3/2	2	3		
Supposed atomic vibration of Batschinski (see p. 178)		1/6	1/2	2/3	1	4/3	5/3	2	7/3	
Refractivity		1/16	1/8	1/4	1	3/2	5/3	2		

These are first crude approximations, and vary where the data are uncertain. They will surely approach more nearly to each other and to Goldschmidt's law of complication with further investigation.

CHAPTER IV.

1. On the Exact Position of the Elements on the Helix.—The

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[1] R. Quintan: L'Eau de Mer Milieu Organique, Paris, 1904 A. C. Lane: Science, **26**, 129 (1907).

horizontal line through hydrogen (see Fig. III) cuts off one-fourth of the second circle in either direction, *Cn H*, which equals unity. The elements occupying positions on this circle may be thought to be exactly fixed in position, and to be very simple, as indicated by low valence, combining weight, density, and by simple spectra.

The continuation of this line cuts off a distance almost equal to 2 on the octave curve, namely, *Cn Li*, which equals 41° 25′; while 45° on this circle equals 2. In the same way this line cuts off on the double octave curve a length of 23° 33′, *Cn K*, while 22° 30′ equals 3. On the last curve the line cuts off *Cn O*, which equals 14° 20′, while 11° 15′ equals 4. This symbolizes the fact that on the larger circles the position of the complex elements is a small area rather than a point, as seen by the slight lack of agreement with the nearest diameters in the diagram where the line cuts each of the larger circles.

Even with this latitude, it is found that when the elements are put in their true relative positions in accordance with the differences of their atomic weights, as in the atomic weight helix described below, the agreement with their ideal positions is much less perfect than might have been expected, and curious and unexpected symmetries come to light (see Fig. X).

It is further found that the elements can be nearly as well placed on the curve by using the successive differences of the densities, as in the density helix below (see Fig. XI), and that the inequalities of the two curves largely counterbalance each other, the first being as much too advanced as the other is retarded. So that a table made by taking the average position indicated by the atomic weight and the density differences, as in the third helix below, brings the elements much nearer the true position (see Fig. XII).

It is then inferred that the distance on the last curve by which each element is separated from its ideal position, taken with opposite sign, would represent the value of the remaining functions (perhaps principally valence) which influence the position of the elements.

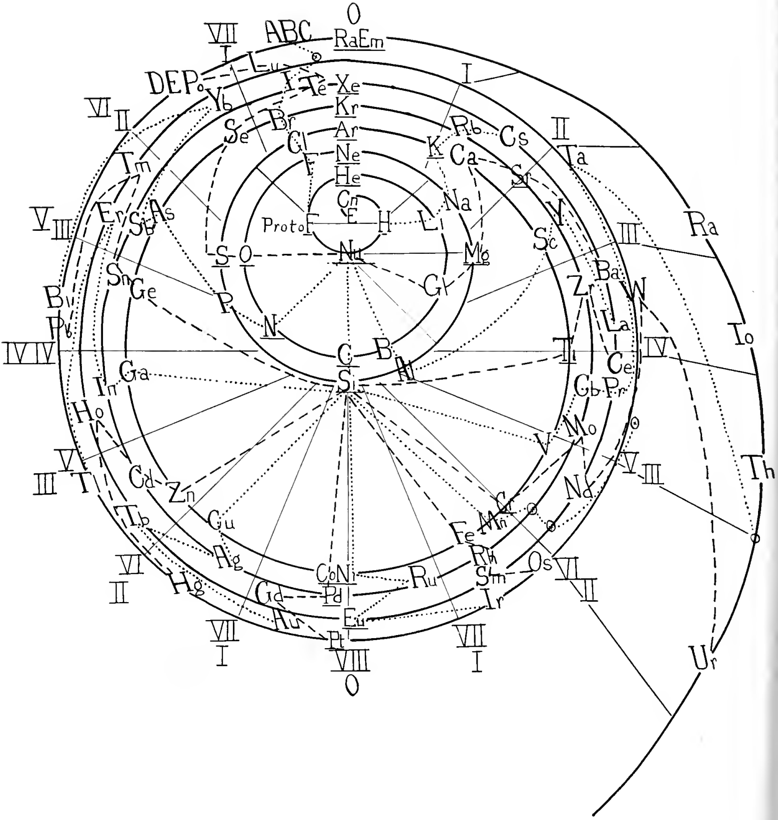

Fig. X.—The Atomic Weight Helix.

The elements are placed upon the helix, in accordance with the real differences between the atomic weights. See page 199.

This brings into clear light the relative importance of valence, atomic weight, density, and the ideal "position." The atomic weights have had a primary value in placing the elements in that natural order, which has brought out their periodic or harmonic relations, and the suggestion of a "position" of ideal symmetry. It has had something of the value of a scaffolding to the completed building.

The density and valence have aided in breaking the curve into its harmonic periods.

Measurement by the atomic weight is something like measurement from the absolute zero, or from the beginning of a journey; measurement of density along the separate groups is like measuring from a fixed zero or from the beginning of each day's journey.

This measuring may be in terms of atomic weight, density, or other harmonic relations, but in the formation of the regular "series" in the periodic table it has been assumed that valence and the ideal "position" number were identical.

Will it be possible to find such values of the valence and other functions as, combined with the values of the above diagram, Fig. XII, will bring the elements into their ideal positions?

2. *The Atomic Weight Helix.*—In Fig. X the elements are put in their true places in accordance with the real interspaces between them found by subtracting each atomic weight from the following one.

All elements which retain the ideal position are underlined.

There is a certain justification for this construction in the fact that when the helix is thus formed the heavy elements at the bottom of the meridian and many at the ends of the horizontal diameter also retain their ideal position.

Since the elements are placed for convenience on circles of gradually increasing size, which yet represent nearly the same advance in atomic weight, the length of each circle was obtained by subtracting the atomic weight of the inert gas at its beginning from that at its end, and with this as a denominator and each interspace as a numerator the proper fraction of 360° was obtained and protracted upon the proper circle. A dotted line connects the elements of each series and shows how far they depart from the ideal position.[1]

The elements are assumed to stand symmetrically in the small hydrogen circle. In the octaves the interspaces are the normal number, 2 or either 1 or 3, and the elements thus occupy either the ideal or the intermediate position.

The elements of the potassium or principal circle are more nearly in place than those of any other of the double octaves. There is developed a perfect meridional symmetry. Cobalt and nickel are nearly in the ideal position together and yet face opposite ways. With curious alternating symmetry a loop goes out in the second circle to ruthenium on the right, and its counterpart goes out to gadolinium in the third circle and to the left.

An inclined N is thus formed, which on the right reaches a minimum expression in the manganese and vanadium lines and rises to a maximum in the calcium line and then decreases slightly. The lines assume inclined M-shapes when, with the chromium line, the radium-uranium elements join the series.

In the second semicircle the M-shaped figure is the counterpart of the preceding and quickly reaches a maximum and in the last line but one fails to return upon itself, thus carrying tellurium far beyond the vertical haloid line, which is abnormally flattened.

The point of first interest is that in the midst of much apparent irregularity, carbon and silicon and one element in each triad occupy exactly the end of the vertical diameter opposite the inert gases, so that all irregularities are compensated within each semicircle, and a fresh start is taken. Thus the irregularities of the descending and of the ascending curve have each its own law, as was seen in the deduction of the laws of condensation.

Unlike all the other groups, the halogens fluorine and chlorine are crowded beyond their proper symmetry position to a point close up to the line of the inert gases, from which they are separated by only a unit interspace, and this and the axial position of the inert gases are the only points in which the octaves and the larger curves show similarity. (See either side of the

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[1] Unknown elements are placed halfway between their neighbors.

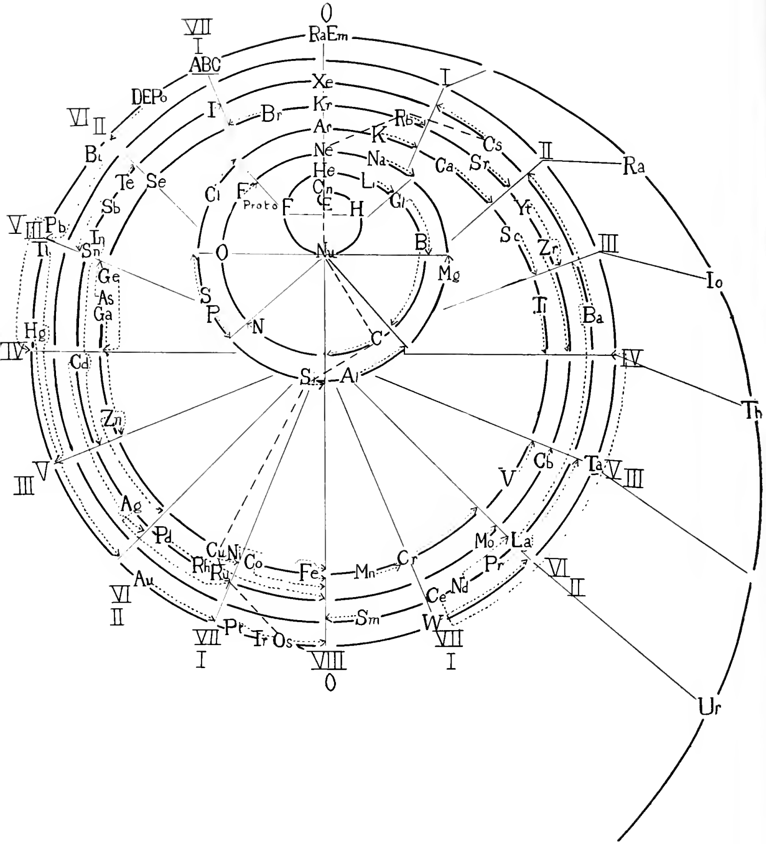

Fig. XI.—The Density Helix.

he elements are put on the helix in accordance with the real differences between the densities and brought into their ideal position by a dotted line (see Chap. IV, page 201).

The upper part of the line of dashes above E is the line of minimum recorded density; the lower part, that of maximum density.

line of the inert gases on Fig. X and the table on page 203).

It is as if all the halogens, moving parallel to each other along their respective circles like a row of runners, had come up to a fixed point, close to the zero line, at the best distance from which to make the jump over this zero line, and as if they had got so much momentum that they landed (like Alice jumping through the looking glass), transformed from most negative acid-makers to most positive alkalies, at points far beyond the line of symmetry, only excepting potassium, the leader of the central circle—the "dominant" of Goldschmidt's law—which landed and halted at the line of symmetry and stands on the circle high above the others, Al-Kali, king of the alkalies.

3. The Density Helix (Fig. XI).—The elements are here placed on the helix in accordance with the interspaces between the successive densities, the inert gases furnishing, as before, the origin of measurement.

A single curious adjustment was required. The abnormal gases, nitrogen and oxygen, which cause the gas area in the octaves to sink into parallelism with the ecliptic line (see Fig. II and page 187) require to be multiplied, nitrogen by 3, and oxygen by 3/2, and they are then brought into their ideal positions.[1] With this exception the elements come into an arrangement similar to and hardly less regular than that obtained above with the atomic weights. There are a few overlaps as in the former curve. The alkalies and the halogens are indeed nearer the ideal place. In the first quadrant there is the same sharp bend forward, exaggerated in the case of barium, lanthanum and cerium. An N-shaped figure directed backwards dominates the second quadrant, which is replaced by an advancing N in the case of iron and in the third quadrant this would probably be continued; but as there are no values known for the elements in the third circle, the N is replaced by an advancing V, which flattens into a straight line as it passes into the fourth octant.

It is to be noted that the line of minimum density is on the

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[1] This may give a hint as to what the density of these elements would be in the solid form.

axis up to neon, but one period to the right in the line of the alkalies from caesium to potassium, while the line of maximum density shifts by the same amount to the left in the case of copper at the other end of the diameter.

4. *The Combined Density-Atomic Weight Helix* (*Fig. XII*).—Assigning to each element the average of its values on the preceding diagrams, a curve is produced that approaches the elements in a marked way to their ideal position. The smaller symbols give the ideal, the slanting ones the real position.

It brings out strongly the fact that the values are largely advanced beyond the ideal position in the atomic weight numbers and the opposite in the density numbers.

5. *The Persistence of the Unit Interspace between the Halogens and Inert Gases and the Combining Weight of Argon.*—The following table, formed by looking down on the helix from above, makes clear the curious interspace relations on either side of the line of inert gases.

The lowest line is hypothetical. In the second to the fourth lines the interspace should be 2 + 2 = 4. It is 1 + 3 = 4.

On the fifth to seventh lines it should be 3 + 3 = 6. In the best measured case, iodine to caesium, it is 1 + 5 = 6.

In the upper or long circle the interspace should be 4 + 4 = 8. It is 1 + 7 = 8, as far as the numbers can be made out in this uncertain region.

The above result is obtained, it will be observed, by changing the atomic weight of argon to 36.

The combining weight of argon is obtained by indirect methods for an element which does not combine, and the determination is much less certain than for chlorine or potassium.

As we obtain the position of neon or xenon by adding 1 to tellurium or iodine, so we should be able to do with argon or krypton. Having done so, we obtain numbers which have the normal interspace relation in the vertical column, about 16 between neon and argon, about 46 b tween the others.

Lord Kelvin has calculated the size of the atom and found 35.62 for the argon molecule.[1] Ramsay has calculated that if five per cent. of the gas were monatomic it would have an atomic weight 36.

[1] Phil. Mag., [6] **4**, 301.

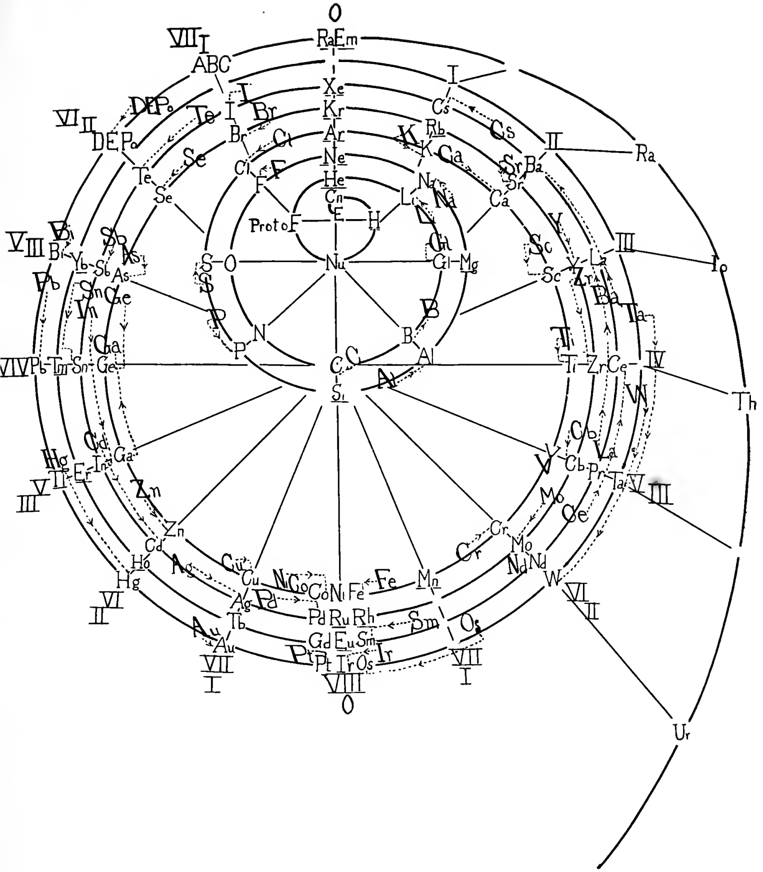

FIG. XII.—The Atomic Weight and Density Helix.

e elements are placed (in larger slanting letters) upon the helix in accordance with the average of their densities and their atomic weights. Those which retain the ideal position are underlined, the others are brought into their proper places by a line of dots.

Halogens with transverse interspaces.	At. wt.	Longitudinal interspaces.	Inert gases with transverse interspaces.	At. wt.	Longitudinal interspaces.	Alkalies with transverse interspaces.	At. wt.
A, B and C emanations	220.0	1.0	Radium emanation	221.0	1.0	(Thorium X)	222.0
45			45			45	
Unknown	175.0	1.0	Unknown	176.0	1.0	Unknown	177.0
48.15			48			44.1	
Iodine	126.85	1.15	Xenon	128.0	4.9	Caesium	132.29
46.89			46.2			47.4	
Bromine	79.96	1.84	Krypton	81.8	3.7	Rubidium	85.5
44.51			45.8			45.35	
Chlorine	35.45	0.55	Argon	36	3.15	Potassium	39.15
16.45			16			16.15	
Fluorine	19.0	1.0	Neon	20.0	3.0	Sodium	23.0
16			16			16	
Protofluorine	3.0	1.0	Helium	4.0	3.0	Lithium	7.0
3			3.7			6	
E	0	0.3	Coronium	0.3	0.7	Hydrogen	1.0

There remains, in connection with the persistence of the unit distance along the whole inert gas series, the fact that the average length of the long circle seems to be near 46 instead of near 48. It seems possible that the interspace before the inert gases which should be 3 is condensed into 1, and that without compensation, thus reducing the whole length from 48 to 46. More weight is probably to be put on the fact that the most accurately determined elements give a number near to 48 (as barium-strontium, strontium-calcium).

CHAPTER VI.

1. Atomic Weight Formulae and Diagrams.—I asked my colleague, Professor T. C. Esty, to consider the formula which would express the curve of the helix, and he assured me that a formula for a disconnected series of five circles would be extremely complex, and would be moreover only useful to deduce just the relations which have already been obtained by observation, as given in the table on page 169.

The ideal relations of the elements as expressed or implied in the complex helix are so harmonic that it is not strange that many have been impelled to search for some equation which would give the atomic weights.

The many empirical equations from which the atomic weight may be approximately deduced seem to depend largely upon the fact that any series of numbers separated by small and varying differences may be represented by many equations which will give the numbers with errors that rarely surpass the difference between the numbers themselves. Thus the latest of these equations,[1] $W = (N + 2)^{1.21}$, where N equals the number representing the position of the given element in the whole list of the elements as arranged in Mendeléeff's table, gives remarkable results, but seems to depend upon the fact that the normal interspaces are two and three in the cases concerned, so that adding two to the position number and increasing it by the small exponent will give generally an approximate result.

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[1] J. H. Vincent: On a Numerical Connection between the Atomic Weights. Phil. Mag., [6] **4**, 103.

All these equations seem to derive their value from the fundamental importance of the position number.

Of all these equations and diagrams, that of Johnstone Stoney is the most wonderful and suggestive.[1] It is indeed particularly suggestive that it was apparently originally rejected by the Council of the Royal Society, and published by its author only after it was found to contain the prophecy of the whole helium series.

On inspection the figure shows that if the two inner circles were coiled with half radius the triads and alkalis would be brought each into a single series; and the need of the curious sesquiradii and the assumption of a logarithmic spiral are avoided.

I cannot refrain from calling the attention of organic chemists to the remarkable right- and left-handed spirals of Thomas Carnelley,[2] who did so much to develop the harmonic relations implied in the periodic law.

He prepared a table of the haloid salts of the organic bases, and showed that these bases, when placed in the order of increasing complexity and combining weight, exhibit a remarkable parallelism with the elements in the periodic table. This was remarkable as suggesting the complexity of the elements. He then arranged the series of organic bases and the elements in similar spirals, much like the diagram of Stoney, and came on the peculiar result that the elements form a right-handed and the organic bases a left-handed spiral.

2. *The Direction of the Growth of the Elements.*—The direction of the devolution of the radio-active elements is usually assumed to be backwards along the curve of the helix, and the direction of evolution is usually assumed to have been along the curve in the order of the increasing complexity of the elements, and this assumption underlies the preceding discussion. This is the order in which the molecules of the elements have been built up by the successive addition of electrons according to J. J. Thompson.[3]

It has been argued in a recent important and baffling paper[4]

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[1] Phil. Mag., [6] **4**, 411 (1902).

[2] The Periodic Law. Chem. News, **53**, 171.

[3] On the Structure of the Atom. Phil. Mag., [6] **7**, 237.

[4] A. C. and A. E. Jessup: Evolution and Devolution of the Elements. Phil. Mag.; [6] **15**, 46.

that evolution was in part radial, and so the elements of each series, as the alkalies, are bound together genetically.

The argument is advanced that, because the nitrogen-bismuth series is wanting in the sun, the whole series has never been developed in the sun, and thus is a series that appears or fails to appear as a unit. Since the spectra of these elements can be detected only with difficulty in the laboratory when metals are present in abundance, the apparent absence of their spectra in the sun cannot be made the basis of any strong argument for the absence[1] of the corresponding elements.

Moreover, the presence of the cyanogen lines would indicate the presence of nitrogen, and the absence of the whole fourth or volatile quadrant except the central elements (see Sec. V, 3, page 195) would connect their absence with their volatility.

Also the order of appearance of the elements, and especially the late appearance of sodium, in the hot stars may better be put among the unexplained phenomena of a difficult subject than as proof of radial evolution.

The argument is advanced that the helium, lithium, glucinum and fluorine series are evolved outwardly in the sense that helium becomes neon, lithium becomes sodium, sodium becomes potassium, and so on. This is called the principle of heredity; that similar elements of like valence should be derived from each other. Thus, for example, barium should be derived from strontium because they are both bivalent and in the same series. This involves the addition of 49.8 in weight to the strontium atom to make barium, and it seems more reasonable to derive it by the small addition of 4.5 from caesium.

Moreover the principal is not carried through consistently, but an unexplained process of "indirect evolution" is introduced, by which the four elements, carbon to fluorine, the ten elements, vanadium to germanium, and many of the heavy metals near copper (indeed, the majority of the elements)

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[1] G. F. Becker: Radio-Activity and Cosmogony. Bull. Geo. Soc., **19**, 113.

are derived from each other in the order of increasing atomic weights, as is ordinarily assumed for all the elements.

The marked harmonic relations existing between the elements of the four series mentioned above to which the "law of heredity" applies find a satisfactory explanation if we assume them to have been derived in the order of their atomic weights like the others.

We may say that sodium is like lithium, barium like strontium, because they are the corresponding notes of the next higher octave, and not because of any principle of derivation or heredity between them, just as there is in music a harmonic relation between the A of one octave and the A of all the other octaves, without there being any proof therefrom that these A's have been derived directly the one from the other.

Indeed, the peculiar equations derived in the article, by which the atomic weights of the beryllium series are calculated, will find application equally well on either method of derivation, whether calcium is derived from magnesium by the immediate addition of 31 in weight, or whether this addition has been made in parts so that several intermediate elements (bismuth, carbon, etc.) have been formed between. In either case there could be an aggregate devolution and "recovery" in alternation.

The complex equations mentioned above[1] are fascinating but inconclusive.

To assume that the average interspace, which, in a large number of careful determinations, averages about 47, should be called 52 because a symmetrical series of arithmetical progression which has no known connection with the matter foots up 52; to set 1.1 = 0.8 and again = 0.6 as the first term of two series of three terms each, where the third term, the position of the element between barium and radium, is assumed to be 34 when if radium is 36.9 it may well be 40, is to take much for granted even in a region so much infested by mathematics as this one is.

The equations are obtained by the further assumption that there is an alternate disintegration and reintegration of

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[1] Devolution and Evolution of the Elements. Phil. Mag., [6] **15**, 47.

the most permanent elements of the series: beryllium, calcium and barium losing from their theoretical values by increasing amounts after the manner of radium, while the intervening elements lose and then gain, but in the case of "protoradium" and radium there is strangely no loss.

The same equations cannot be applied to or derived from the other series, and the many remarkable relations adduced remain largely unexplained.

SECTION VIII—EVOLUTION AND DEVOLUTION.

The helix is a working model and it suggests that there is only one enduring stable assemblage of corpuscles between the "Urstoff" and hydrogen with its thousand corpuscles, and if that element be coronium, it has endured only under the exceptional conditions of the corona.

As the *vix generatrix* passed over each unit space in the first circle the conditions favored the formation of a new element. In this circle are the simplest forms of matter from hydrogen to helium. They appear abundantly in the nebulae; existing, and perhaps formed, near the absolute zero, where no heat vibrations could yet be predicted, and where unexplained electrical activities could cause the light of the nebulae. The helix prophesies the discovery of only one new element of low atomic weight, protofluorine.

On the completion of the first circle, a double momentum swelled the curve to a full octave culminating in the unique element carbon, the element of life, and in a second octave culminating in silicon, the basis of the rocks. In contrast to the corpuscular temperature or vibration within the atom in the elements of the nebulae, normal molecular vibration and normal electrical conditions become prevalent.

On passing potassium the treble momentum culminated in a double octave with the iron-nickel-cobalt group of the hot stars, the meteorites and the interior of the earth (see top of Fig. I). One may surmise that most of the heavy elements beyond this group are unimportant in the mass of the earth as they are in the meteorites. A considerable molecular radiation may have been a condition precedent to the addition of a group of corpuscles equivalent to three hydrogen atoms, and the increasing complexity of the elements is indicated by their high and varying valence. Will three new elements be found to fill the gap below manganese, or will the outer triads be robbed for this purpose? The almost empty semicircle between ytterbium and tantalum is tantalizing, but the symmetry of the helix would rule out the gathering of the elements of the rare earths into a group like the triads, as has been suggested.

The sun carries the evolution a step further and it is conceivable that all the elements of the lowest-fusing quadrant have evaporated from it. Lead alone of the very heavy elements appears in the sun as a sort of "calx" or "caput mortuum," suggesting that evaporation into helium has reached its limit there. It is remarkable that at the farthest place from this quadrant, at the outermost curve of the high-fusing semicircle, the radium elements should be evaporating with explosive heat- and light-giving violence over all the surface of the earth, should exist in the outer layers of the earth only, and should be brought up by the light and highly acid pegmatite, whose quartz grains have been formed below 800°.[1] Becker's suggestion of the genesis of pegmatite with uranium as a potentializer of the energy that must escape in its formation is most interesting.[2]

When the assemblages had become so complex that devolution began to prevail over evolution, the size of the added group of corpuscles was increased to four, and a short advance only was made along the first quadruple-octave ring.

If ink is allowed to flow from a dropping tube, the point of which is immersed in water in a tall glass, the descending stream soon forms vortex rings and, as these rings sink and expand, they often become scalloped at the edges and the scallops expand in lobes which separate in distinct subordinate vortex rings while the central part closes in as an almost perfect ring again. Sometimes several of these lobes will separate symmetrically at the same time like the fluting on the border

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[1] Day and Shepard: Am. J. Sci., **20**, 276 (1906).

[2] *Loc. cit.*, p. 143.

of a rose leaf. This is a model of the radium emanations and of the breaking up of the complex atoms. Thus is the limit set to the complexity of the atom and the length of the helix.

It has a mystical attractiveness that the helix has a shape like the spiral nebula from which all things have been thought to originate, and toward which they again tend, and that the tetrahedral element carbon stands in the center of this helix and by its shape (ranging from the tetrahedron, which includes the smallest amount of matter in unit surface, almost to the sphere, which contains the largest amount of matter in unit surface) typifies the infinite possibilities of life, of which it is the vehicle, and embodies the tetrahedral form which the earth has repeatedly, if imperfectly, approached.[1]

Furthermore the helix is a curious parallel of the solar system itself. They are both ring systems and, for the four small ring, there are the four small inner planets, and the two smallest rings match the two inner moonless planets.

For the four large rings there are the four large outer planets and as Jupiter, the first of them, is the culmination of the solar system, so the first large ring is the culmination of the elemental system, and furnishes in potassium, calcium, the iron group, etc., the major part of the basic elements for the meteorites, the earth, and perhaps for the whole planetary assemblage.

For the larger partial ring there stands the possibility of an outer planet.

OBITUARIES.

RUDOLPH FITTIG.

After a brief illness Rudolph Fittig died November 19, 1910. He was born at Hamburg, Germany, December 6, 1835, and was therefore nearly seventy-five years old at the time of his death. Fittig studied at Göttingen from 1856 to 1859. The moving spirit in the Göttingen laboratory at that time was, of course, Wöhler, whose chief interest was in inorganic chemistry. Limpricht had general charge of organic chemistry, and it was under him that Fittig did most of his work.

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[1] T. Arldt: "Die Entwickelung der Erde" (1907), p. 506.

Among his contemporaries were Beilstein and Hübner. When Limpricht went to Greifswald, Beilstein had already gone to St. Petersburg, and this left the two young men, Fittig and Hübner, to take care of organic chemistry. Fittig became Privatdocent in 1860, and in 1866 he was made Professor *extraordinarius*. In 1870 he was called to Tübingen to take the place of Strecker, who had gone to Würzburg. He remained at Tübingen until 1876, when he accepted the professorship of chemistry in the University of Strassburg as the successor of Von Baeyer, who had been called to Munich. He performed the duties of the professorship in Strassburg until 1902, when he retired from active service, though he continued to live in Strassburg and occupied himself in rounding out his extensive investigations and preparing the results for publication. His work never stopped until his death, as far as the outside world can judge.

Fittig began his career as an investigator by some observations on acetone. He soon became interested in the aromatic compounds which were then coming into prominence. Nothing of much importance came of his work, however, until 1864, when his famous article, "The Synthesis of Methyl-phenyl by the Würtz Method", appeared in the *Annalen der Chemie.*[1] Tollens was associated with him in this piece of work and the article appeared under both names. Benzene had then been known for a number of years, but no helpful suggestion had up to that time been made regarding its relations to the paraffins. Toluene was also known and had received its place next to benzene in the aromatic series, but the relation between benzene and toluene was not at all clear to the chemists of that day. That the two differed from each other in composition as the successive members of an homologous series differ from each other was recognized, but the nature of homology was still a subject of discussion, and the question whether the then known toluene was a true homologue of benzene was unanswered. Würtz had devised a method of synthesis for the paraffins which has proved of great value in clearing up the relations between these hydrocarbons, and it occurred to Fittig to apply this method to the aromatic hydrocarbons. He first treated monobrombenzene with sodium and found that the bromine is easily removed, and that the two phenyl groups thus formed unite to form diphenyl:

$$2C_6H_5Br + 2Na = C_6H_5—C_6H_5 + 2NaBr.$$

The fact having been established that sodium has the power

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[1] Vol. **131**, 303.

to remove the bromine from monobrombenzene, he next tried the action of sodium on a mixture of monobrombenzene and methyl bromide. The reaction took place as was expected, and a compound to which Fittig and Tollens gave the name methyl-phenyl was formed:

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5\text{—}CH_3 + 2NaBr.$$

They showed that their synthetical product was identical with toluene, and in discussing the result they used these words: "Accordingly toluene is benzene in which the radical methyl has been substituted for an atom of hydrogen." * * "Toluene is generally regarded as the second member of the benzene series, that is to say, as a true homologue of benzene. If this view is correct, the possibility is given of building up an homologous series from the initial member by means of such synthetical experiments, and, we may say, in general, that one substance is homologous to another, if in place of hydrogen in its radical it contains the radical methyl. Before, however, we can accept such a view in regard to the constitution of homologous compounds as correct, the question must first be answered, whether toluene really is a homologue of benzene, whether it bears to benzene the same relation, that, for example, ethyl compounds bear to methyl compounds. The conduct of the two hydrocarbons as far as it is at present known is well calculated to give a negative, rather than a positive, answer to the question."

This passage is very interesting historically, as it helps us to understand how our present clear-cut view of homology came to be accepted. Very shortly after the appearance of the article by Fittig and Tollens, Schorlemmer[1] showed that the compound made by extracting the chlorine from methyl chloride is identical with "ethyl hydride," that it is in fact ethane, the second member of the paraffin series. This result, taken together with that obtained by Fittig and Tollens, left no doubt in regard to the nature of homology, and since that time it has been glibly defined with little thought, generally speaking, as to how the explanation was reached. Fittig seems to have lost his doubts regarding the homology of toluene and benzene.

In 1866 Kekulé, in his famous article on aromatic compounds,[2] refers to Fittig's work thus: "The beautiful investigations of Fittig leave no room for doubt in regard to the constitution of these hydrocarbons." And much later,

[1] Ann. Chem. (Liebig), **132**, 234.

[2] *Ibid.*, **137**, 1141.

in 1890, when the German Chemical Society celebrated the 25th anniversary of the birth of his benzene theory, Kekulé again referred to Fittig's work. He tells of the way his theory of the constitution of chemical compounds came to him in a half-dreamy state and how he had put aside what he had written on this subject at that time. He then adds: "The same thing happened with the benzene theory. It lay nearly a year written out among my papers, until the beautiful synthesis of the aromatic hydrocarbons by Fittig and Tollens led me to publish what I had written."

The next important contribution of Fittig was one which showed mesitylene to be a trimethyl derivative of benzene. The two articles embodying the results of the investigation on mesitylene appeared in the *Annalen* in 1867 and 1868. He showed that by oxidation mesitylene yields successively a monobasic, a dibasic, and a tribasic acid, and that each stage involves the conversion of one methyl group into carboxyl. From the tribasic acid by distillation with lime benzene is formed, from the dibasic acid toluene is formed in the same way, and from the monobasic acid one of the xylenes. He says: "It follows, however, from the facts that mesitylene is a true trimethylbenzene, and that the following constitutional formulas must be assigned to the principal members of the mesitylene series:

$$\begin{array}{cccc}
C_6H_3\left\{\begin{array}{l}CH_3\\ CH_3\\ CH_3\end{array}\right. & C_6H_3\left\{\begin{array}{l}CH_3\\ CH_3\\ COOH\end{array}\right. & C_6H_3\left\{\begin{array}{l}CH_3\\ COOH\\ COOH\end{array}\right. & C_6H_3\left\{\begin{array}{l}COOH\\ COOH\\ COOH\end{array}\right. \\
\text{Mesitylene.} & \text{Mesitylenic acid.} & \text{Uvitic acid.} & \text{Trimesitic acid.}
\end{array}$$

Later it was shown that mesitylene is the symmetrical variety of trimethylbenzene and, that being established, it follows that the xylene obtained from mesitylenic acid must be the meta variety, and this becomes one of the fundamental facts upon which the classification of the di-substitution products of benzene into ortho, meta, and para rests.

It will be quite impossible to discuss all of Fittig's work as the two important contributions above referred to have been discussed. Indeed it is doubtful whether anything he did in the years after 1868 had as much influence on chemical thought as that which he did before this time.

It has already been stated that he was called to Tübingen in 1870. There he found conditions somewhat unfavorable. He had to do more lecturing and the laboratory was a sorry affair. Fittig had the most fastidious tastes so far as his laboratory surroundings were concerned. He was extremely neat and orderly. In Tübingen things looked down at the heel and this seemed to worry him constantly. Nevertheless he went on with his work and accomplished much. During the six years of his life here he was rather feeling his way. Nothing very striking came of it. His work on phenanthrene led him to the view that the quinones are diketones and this view prevails at present. An investigation on sorbic acid and another on piperic acid interested him in unsaturated acids and these continued to occupy him several years. The results are embodied in a series of articles entitled "Untersuchungen über die ungesättigten Säuren," the first of which appeared in the *Annalen* in 1877 and the last in 1883.

His discovery of the lactones and the lactonic acids was announced in 1880 and a number of comprehensive articles on these compounds followed, extending to 1893.

His studies of the unsaturated acids led, among other things, to the interesting observation that some of these acids are subject to an internal change involving a "shifting of the double bond."

By invitation of the German Chemical Society, he gave a general account of his work on the unsaturated acids before the Society October 15, 1894. The address was published in the *Berichte*.[1] He tells in an interesting way how he came to take up this work and in general what object he had in view. The following characteristic passage may be quoted to advantage. He says: "My colleagues have repeatedly said to me that it is difficult to work through my bulky articles, and I believe many have asked whether it was necessary to collect such a mass of material and always to test the same reaction in so many special cases. Gentlemen, I can assure you that the preparation of new chemical compounds has never in my life had any attraction for me. When, however, I formed the plan for these investigations and spoke with my friends about it, I knew very well that the carrying out of the plan would require many years, for it was perfectly clear to me that no generalizations could be reached through the study of a few cases."

At the beginning of Fittig's work the field of the unsaturated acids was almost uncultivated. He has enriched it with almost innumerable discoveries and it has yielded an abundant harvest.

Fittig's work was characterized by great thoroughness and accuracy and he justly prided himself upon the fact that no one had ever convicted him of an experimental error! There

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[1] Vol. **27**, 2658.

was, to be sure, a painful polemic between him and Wislicenus in regard to the bromine addition-product of angelic acid, but it turned out that the difference between the results obtained by the two observers was due to the fact that one worked on the south side of his laboratory, the other on the north side, and the light proved to be the determining factor in the reaction.

Fittig did not directly contribute to any extent to the theories of chemistry, though he furnished the material basis for profitable speculation, notably, as has been pointed out, in his earliest work on aromatic compounds. It is doubtful whether any text-book of chemistry has ever been written that had less reference to underlying theories than his "Grundriss der anorganischen Chemie" and his editions of "Wöhler's Grundriss der organischen Chemie." These books are made up of compact statements of facts and are extremely valuable for the purpose for which they were prepared. He was a clear lecturer and an excellent laboratory teacher. His insistence upon thoroughness was characteristic of everything he did, and those who had the privilege of working under him have every reason to be thankful for the influence exerted by him as a teacher. The writer of the sketch was closely associated with Fittig for four years, two years as a student at Göttingen and two years as assistant at Tübingen, and he always recalls these years with gratitude, conscious of the fact that this association played a large part in such intellectual regeneration as he has been permitted to experience.

IRA REMSEN.

FELIX B. AHRENS.

Felix B. Ahrens, Professor of Agricultural and Chemical Technology at the University of Breslau, founder and for fifteen years editor of the collection of chemical and chemical-technological monographs which bears his name, died November 14th after an illness of almost two years.

Ahrens was born in Danzig on October 23, 1863, and was therefore only 47 years old at the time of his death. He went to Berlin in 1882, intending to become a pharmacist, but a few years later he took up the study of chemistry in the university there and in 1886 received his Doctor's degree from the University of Breslau. He studied under Ladenburg for a time at Kiel, and was also an assistant under Ferdinand Cohn in the Institute of Plant Physiology at Breslau. From 1890 to 1894, he was first assistant in the Chemical Institute of the University of Breslau, when he was promoted to the chair which he occupied till his health compelled him to retire from active work in 1908. While with Ladenburg, he carried out important investigations on the alkaloids. His later work was devoted chiefly to technical problems, and his contributions on coal tar, acetylene and the sulphite liquors are worthy of note. He had a peculiar gift for putting important scientific advances into popular language and also contributed largely to Ladenburg's Dictionary of Chemistry and other compilatory works. Under his guidance, his "Sammlung" has achieved a success which assures the continuance of this series of valuable monographs, each of which is written by an acknowledged authority in his field.

STANISLAUS VON KOSTANECKI.

On November 15th, Stanislaus von Kostanecki, widely known for his investigations on natural coloring substances, died from the effects of a painful operation he had undergone a few days before. He was only a little over 50 years old, having been born in Myszaków, Russian Poland, April 16, 1860. His first chemical training was received at the hands of Prof. Krug, at Posen, and in 1881 he went to Berlin where he came under the influence of Finkener and Liebermann. The latter made him his assistant in 1884 and together they published a number of important papers, that on "Oxyanthraquinone," especially, attracting wide attention. In 1886 he went to Mülhausen as Noetling's assistant, where he displayed such originality and activity that in 1890, when barely 30 years old, he was appointed "Ordinarius" at Berne and in three years had so built up his department that a new building had to be erected to accommodate the students flocking in ever-increasing numbers to his laboratory. Among his more important investigations may be mentioned the synthesis of gentisin and other natural coloring substances and the preparation of the mother substances, chromone, flavone and flavonole, and the exhaustive study of brasilin and curcumin. In 1903 he was awarded the Lavoisier medal by the French Chemical Society, and the Mülhausen Industrial Society gave him its gold medal. He was a member of the Krakau Academy of Sciences, a "Chevalier" of the Legion of Honor, an ex-officer of the German Chemical Society, and president of the Swiss Chemical Society. His activity continued unabated almost to the very day of his death and during the last summer he published three papers.

REVIEWS.

Die Gewinnung des Broms in der Kaliindustrie. Von Dr. Phil, Max Mitreiter, Betriebschemiker. Monographien über chemisch-technische Fabrikations-Methoden. Band XX. Mit 24 in den Text gedruckten Abbildungen. Halle a. S.: Wilhelm Knapp. 1910. pp. 54. Price, M. 2.

The technical production of bromine is confined to the United States and to Germany. When Frank, in 1865, began the technical production, the price was $23.00 per kilogram. It has fallen as low as 16 cents, and is now about forty cents.

The raw material utilized for the production of bromine in the potash works is the mother liquor resulting from the separation of potassium chloride from carnallite; it contains 0.2 to 0.3 per cent. magnesium bromide and the bromine is obtained by the chemical method or by electrolysis. In the chemical method the bromine is liberated by the action of chlorine on magnesium bromide. The work is carried on in the apparatus of Wünsche which involves the use of iron bromide, Fe_3Br_8, in refining the bromine, or by the newer method of Kubierschky; in this process a mixture of gaseous chlorine and bromine issues from the apparatus in which the carnallite mother-liquor is treated with chlorine and is conducted into a refining apparatus in which by simple distillation it is separated into its two components of different vapor tension. For the theory and description of this very ingenious, economical and interesting process, the monograph must be consulted.

The electrolysis of the magnesium bromide is difficult because the amount of this salt in the mother liquor is so small. The methods first adopted have been abandoned; only one method is now in practical use, though the author describes two others as promising; the whole subject seems to be as yet in the experimental stage.

The process in use is that of Kossuth. The apparatus consists of stone-ware vats about four feet long, two wide and one deep, in which thirty-three carbon slabs are so placed that every portion of the liquid in its passage through the vat must come in contact with the electrodes. The magnesium bromide and a small amount of magnesium chloride are electrolyzed; the chlorine resulting from the latter salt displaces bromine in the bromide. The bromine remains dissolved in the liquid and is separated by fractional distillation.

Much bromine is marketed as iron bromide, Fe_3Br_8, which is to bromine what bleaching powder is to chlorine—a convenient carrier; it is sold in this form to the chemical factories where it is employed for making potassium, sodium and ammonium bromides. The Stassfurt works prepare free bromine, iron bromide and "brom-salt." This substance is used in large quantities in the extraction of gold from its ores and consists of a mixture of one equivalent of sodium bromate and two of sodium bromide; by the action of bromine on concentrated sodium hydroxide the mixture $NaBrO_3 + 5NaBr$ results, and this is mixed with more sodium bromate (made in other factories by electrolysis of sodium bromide) to obtain the proportion $NaBrO_3 + 2NaBr$.

The monograph is one of the most interesting of this series and will repay study.

E. R.

Die Chemie der Cellulose, unter besonderer Berücksichtigung der Textil- und Zellstoffindustrien. Von Dr. Phil. Carl G. Schwalbe, a.o. Professor an der Grossh Techn. Hochschule zu Darmstadt. Erste Hälfte. Berlin: Verlag von Gebrüder Borntraeger. 1910. pp. 272. Price, M. 9.60.

To those interested in the chemistry of cellulose, Professor Schwalbe's book will be a welcome addition to the few really good books on the subject.

Since Cross and Bevan wrote their "Cellulose" and "Researches," a large amount of work has been done on cellulose, and to a considerable extent this work has been published in scattered fragments in journals widely different in character and many in number. The peculiar merit of Professor Schwalbe's book is the bringing together of this large number of separate bits of work and coördinating them in a systematic study of the field as now known.

When one notes that there are nearly eleven hundred references to original work in this first half of 272 pages, the force of the statement about the collecting of others' work becomes apparent.

He has of course gone back much further than the recent work in his search—indeed usually to the very beginning.

This material is systematically arranged, so that the book becomes of great value as a means of looking up original work.

The book is of course much more than a mere collection of the work of others. It represents the thought and judgment of Professor Schwalbe and his interpretation of the results of research, together with contributions of his own to the work. His personal opinion in disputed points is always quite evident, but opposing views are fairly stated on the whole.

The reviewer heartily recommends the book to all interested in the chemistry of cellulose, and looks forward to the appearance of the second half of the work with great interest.

George S. Tilley.

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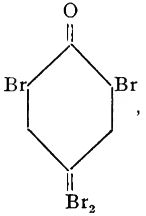
ON THE CONVERSION OF BENZENESULPHONEDIBROMAMIDE INTO DIBROMBENZENESULPHONAMIDE BY MEANS OF CONCENTRATED SULPHURIC ACID.

By J. H. Kastle.

According to our present conceptions tribromphenol bromide and benzenesulphonedibromamide exhibit no analogies as to chemical constitution. Thus, according to Thiele and Eichwede[1] the former is a quinone derivative having the constitution



whereas benzenesulphonedibromamide,[2] as its name indicates,

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[1] Ber. d. chem. Ges., **33**, 673 (1900).

[2] Benzenesulphonedibromamide was discovered by Hoogewerff and Van Dorp (Rec. trav. chim., **6**, 373 (1877)). It was afterwards prepared and studied by Kastle, Keiser and Bradley (This Journal, **18**, 4 (1896)) and still more recently by Chattaway (J. Chem. Soc., **87**, 145–171 (1905)). From a mixture of alcohol and water it crystallizes in lustrous, orange-yellow plates, melting at 110° and from chloroform in crystals melting at 116°.

is a *N*-dibrom substitution product of benzenesulphonamide, having the formula $C_6H_5SO_2N.Br_2$.[1] As a matter of fact, however, these two compounds exhibit many analogies in physical and chemical conduct. Both are yellow in color, both melt within the same range of temperature, both are insoluble in water, but soluble in chloroform and other organic solvents. Both contain active bromine, both are unstable at temperatures slightly above their melting points. Both give up bromine slowly even at ordinary temperatures, under ordinary atmospheric conditions. Both readily liberate iodine from potassium iodide.

The most interesting change of which tribromphenol bromide is capable, however, is that under the influence of concentrated sulphuric acid it undergoes a molecular rearrangement whereby it is transformed quantitatively into tetrabromphenol.[2] According to Lobry de Bruyn,[3] sulphur trioxide, and not sulphuric acid *per se*, is the agent primarily responsible for this transformation.

In view, therefore, of the many analogies displayed by tribromphenol bromide and benzenesulphonedibromamide, it seemed not unlikely that like the former the latter would also undergo a molecular rearrangement on treatment with concentrated sulphuric acid.

As a matter of fact, it has long since been pointed out by Chattaway and Orton[4] that substitution by the halogens in the benzene nucleus of aromatic amines and amides of the aromatic carboxylic acids is not a direct process, but one which takes place in two stages, in the first of which the hydrogen attached to the nitrogen is replaced by the halogen, the substituted halides thus produced then undergoing molecular rearrangement, with transfer of halogen to the benzene nucleus. Later Chattaway[5] and his coworkers succeeded in isolating

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[1] This Journal, **18,** 4 (1896). See also Chattaway: J. Chem. Soc., **87,** 163 (1905).

[2] See Benedikt: Ann. Chem. (Liebig), **199,** 127; and also Kastle: This Journal, **27,** 43–52 (1902).

[3] The reference to Lobry de Bruyn's work on this subject is inaccessible to me at the present time.

[4] J. Chem. Soc., **75,** 1046 (1899); **77,** 134, 789, 797, and 800 (1909), etc.; see also Chattaway: *Ibid.*, **86,** 1181 (1904).

[5] J. Chem. Soc., **86,** 1181, 1187 (1904).

many of these substituted nitrogen halides. They also succeeded in showing that many of these compounds could be preserved indefinitely under proper conditions, but that under the influence of catalysts, such as hydrochloric acid in glacial acetic acid, they are readily transformed into ortho and para benzene substitution products.

Cohen[1] and his coworkers also have studied the action of sodium hypochlorite on the sulphonanilides and have arrived at the conclusion that the ultimate formation of *o*- and *p*-chlor substitution products is preceded by the production of *N*-chlor derivatives of the sulphonanilides. So far as I have been able to discover, however, no one has ever accomplished the molecular rearrangement of benzenesulphonedibromamide. In fact, according to Chattaway,[2] the *N*-halogen derivatives of the sulphonamides seem to possess greater stability than the corresponding derivatives of the aromatic carboxylic amides. It, therefore, seemed all the more desirable to see whether molecular rearrangement of benzenesulphonedibromamide could be accomplished by means of concentrated sulphuric acid.

As a matter of fact it has been found that, at ordinary temperature, benzenesulphonedibromamide reacts instantly and somewhat vigorously with concentrated sulphuric acid. Only traces of bromine were liberated and the product of the reaction gave only traces of silver bromide on the addition of silver nitrate.

In my first experiment one gram of finely powdered benzenesulphonedibromamide was added in small amounts at a time, and with immediate mixing, to about 10 cc. of concentrated sulphuric acid. When larger amounts are added to the sulphuric acid the reaction takes place almost explosively and with the evolution of small amounts of bromine. The product of the reaction was poured into water. A white crystalline precipitate separated at once. This was removed by filtration and purified by crystallization from boiling water to which a small amount of animal charcoal had been

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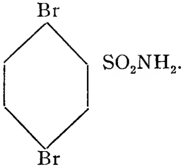
[1] J. Chem. Soc., **85**, 371–378 (1904).

[2] *Ibid.*, **87**, 145–171 (1905).

added. In this way there was obtained 0.5 gram of a white crystalline substance having the general properties of a sulphonamide. It was further purified by recrystallization from hot 95 per cent. alcohol. From this solvent it was obtained in the form of small, compact, glittering crystals, which under the low power of the microscope were observed to consist of well-defined, colorless, transparent, prismatic crystals. These were found to melt at 194°. For 0.2005 gram, heated with pure calcium oxide, were required 12.7 cc. 0.1 N silver nitrate, equivalent to 0.1015 gram bromine, or 50.62 per cent.; calculated for $C_6H_3Br_2SO_2NH_2$, 50.75 per cent.

On heating with lime considerable amounts of ammonia were evolved. There is no doubt, therefore, that this compound is a dibrombenzenesulphonamide, $C_6H_3Br_2SO_2NH_2$. Furthermore, it is more than likely that it is the *p*-dibrombenzenesulphonamide,  This compound melts at 193°. On the other hand, the 1,3,4-dibrombenzenesulphonamide melts at 190°, so that further work will be required to settle definitely the constitution of the dibromsulphonamide resulting from the molecular rearrangement of benzenesulphonedibromamide. A second experiment was carried out in the following manner: Ten cc. of pure concentrated sulphuric acid were cooled to 0° and poured into a large porcelain dish which was placed on cracked ice. To this cold sulphuric acid there was added, in small amounts at a time, 4 grams of benzenesulphonedibromamide. As fast as the dibromamide was added it was intimately rubbed into the sulphuric acid with a porcelain pestle. In this way a mixture was obtained having the color and much the consistency of the yolk of an egg. After all of the dibromamide had been mixed with the sulphuric acid the dish was removed from the ice to the laboratory table and it and its contents allowed gradually to come to ordinary temperature. As a result of this slight rise of temperature the yellow dibromamide gradually dissolved in the concentrated sulphuric acid, giving rise to a clear light brown solution. In a short time, however, white crystals began to separate from the clear brownish solution, so that after 15 to 30 minutes the contents of the dish consisted of a white pasty mass of crystals. This pasty material was then poured into about ten times its volume of water and the white crystalline material thus obtained was collected on the filter and purified by recrystallization from hot water. This experiment was designed primarily to determine more accurately the quantity of dibrombenzenesulphonamide produced from a given amount of the sulphonedibromamide. Unfortunately the greater amount of this was lost during its purification by the breaking of a beaker. As nearly as I could judge from the bulk of the material, however, the dibrombenzenesulphonamide had been formed in large amounts and it is certainly the principal product of the change here under investigation.

As I have already pointed out, the filtrate from the dibrombenzenesulphonamide resulting from this rearrangement of the benzenesulphonedibromamide gives only a slight opalescence with silver nitrate, indicating the absence of hydrobromic acid or bromides. On evaporating this filtrate on the water bath, however, a small amount of a white crystalline substance was obtained. This substance is more easily soluble in water than the dibrombenzenesulphonamide above described. It melts at 135°–140° and also shows signs of fusion during its recrystallization from hot water. This compound has been found to contain only 36 per cent. of bromine. It also gives off ammonia on heating with lime. Up to the present, however, it has not been obtained in sufficient quantity to permit of its identification. Regardless of the nature of this second product, however, it is evident from these results that benzenesulphonedibromamide is largely converted into a dibrombenzenesulphonamide through the action of sulphuric acid. Such a change is of interest from several standpoints. I, therefore, hope to continue this investigation.

UNIVERSITY OF VIRGINIA,
January, 1911.

ON THE REACTION OF IODACETONITRILE WITH SILVER NITRATE.

By S. K. Loy and S. F. Acree.

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

Recent work[1] in this laboratory on the mechanism of the reactions of alkyl halides with urazoles, thiourazoles, and salts of these substances, and with sodium ethylate and sodium phenolate, has shown that in some cases the *anions* of the urazoles are the *chief* substances reacting with the alkyl halides. It appeared probable that the anion first unites with the alkyl halide and forms a complex anion[2] which then decomposes as follows:

$$\text{I. } CH_3I + \overset{+}{Ag} + \overset{-}{NO_3} \rightleftarrows \underset{\text{trace}}{CH_3I.\overset{-}{NO_3}} + \overset{+}{Ag} \longrightarrow CH_3NO_3 + \overset{+}{Ag} + \overset{-}{I}.$$

$$\text{II. } CH_3I + \left\{\begin{matrix} AgNO_3 \\ \text{or} \\ \overset{+}{Ag} + \overset{-}{NO_3} \end{matrix}\right\} \rightleftarrows \underset{\text{trace}}{CH_3I.AgNO_3} \longrightarrow CH_3NO_3 + AgI.$$

But in the case of certain thiourazole salts, of sodium ethylate and of sodium phenolate, Dr. F. M. Rogers, Dr. H. C. Robertson, and Mr. E. K. Marshall have found in work not yet described that the total reaction velocity can be expressed in terms of the concentrations of both the anions (reaction I) and the undissociated salts (reaction II). It had already been shown by Shadinger and Acree[3] that the alkyl halide probably reacts as a molecule with the urazole salts and ap-

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[1] Ber. d. chem. Ges., **41**, 3199 and earlier papers. This Journal, **43**, 505; **44**, 219.

[2] We are glad to mention that our colleague, Professor Heinrich Goldschmidt, has recently come to similar conclusions as a result of his researches on the alkylation of oximes, and has pointed out our prior views and experimental results (Z. Elek. Chem., **14**, 581; **15**, 10. Shepherd: Dissertation, Christiania, 1909). Professor Arthur Lapworth has held similar views for a number of years and has made them the basis of numerous important investigations (J. Chem. Soc., **81**, 1512; **85**, 48; **93**, 30).

[3] This Journal, **39**, 236–248.

parently not as alkyl and iodide ions, as assumed by Bruyn and Steger,[1] nor as alkylidine and hydroiodic acid, as was supposed by Nef,[2] nor yet through the formation of a complex cation as was postulated by Euler.[3] The reaction of these nonionized[4] forms of the salts and alkyl halides had been foreshadowed, theoretically and experimentally, by Johnson and Acree,[5] who found that the transformation of acetylchloraminobenzene in the presence of hydrochloric acid takes place apparently almost entirely through the preliminary formation of an undissociated salt as follows:

$$\mathrm{CH_3CONClC_6H_5} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} \longrightarrow \mathrm{CH_3CONHCl_2C_6H_5} \longrightarrow \mathrm{CH_3CONHC_6H_4Cl} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}}.$$

Shadinger and Acree[6] showed that in certain urazole reactions there could be at most only traces of the complex salt indicated in reactions I and II. It seems highly desirable to learn whether in any case evidence can be secured which proves beyond question that an appreciable amount of such a salt exists and we have taken up this study again. We have chosen this time the double compound obtained by Scholl and Steinkopf[7] by the action of iodacetonitrile on silver nitrate:

$$\mathrm{ICH_2CN} + \mathrm{AgNO_3} \longleftrightarrow \mathrm{AgNO_3.ICH_2CN} \longrightarrow \mathrm{AgI} + \mathrm{NO_3CH_2CN}.$$

This double compound exhibits in a qualitative way all of the properties demanded by the theory of reactions I and II,

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[1] Rec. trav. chim., **18**, 325.

[2] Ann. Chem. (Liebig), **298**, 202–374; **309**, 126; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191.

[3] Ber. d. chem. Ges., **39**, 2734.

[4] For the sake of simplicity we shall use the expressions "reactions of the ions or of the nonionized salts" instead of the more complex expressions involving the idea of a reaction velocity proportional to a constant and to the concentration of the ions or of the nonionized salt. There may be many steps involved in the change of the anion, or of this nonionized salt, into the end products, some of which will be discussed in our full reports.

[5] THIS JOURNAL, **38**, 265; **41**, 461, and especially footnote 3, p. 462.

[6] *Ibid.*, **39**, 275–276.

[7] Ber. d. chem. Ges., **39**, 4393.

in that it can be easily converted back into the silver nitrate and iodacetonitrile, while, on the other hand, it can also be changed, even in the solid state, into silver iodide and cyanmethyl nitrate. The unsaturated nitrile group may aid in making the substance more stable. Professor Scholl kindly left to us the quantitative study of this question.

We have again chosen, as did Shadinger, the conductivity method in studying this problem, the assumption being that the complex salt is not more highly ionized than the silver nitrate, and that the complex ion, $\overline{NO_3}.ICH_2CN$, must necessarily migrate more slowly than the simple nitrate ion. If these two reasonable assumptions hold, and if the complex salt is actually formed and decomposes slowly enough to be studied, we should have a lowering of the conductivity when we introduce iodacetonitrile into standard solutions of silver nitrate, the extent of the lowering depending upon the amount of complex salt formed. Of course, other methods should be used also to study this problem; namely, those involving the lowering of the freezing point, the rise in boiling point, the use of partition methods, the study of the ionic velocities, the use of electromotive force measurements,[1] etc., and we shall later use these. The data secured, however, if trustworthy, show that no appreciable amount of the double salt, $AgNO_3.ICH_2CN$, can be present when solutions of silver nitrate and iodacetonitrile in water, alcohol or acetone are mixed. This harmonizes with the kinetic data which others in this laboratory have obtained in all cases, and if this double salt, or its anion, yields the end products, the small amount present must decompose with a high velocity.

We shall continue to look for the presence of such double compounds in all of our studies, and shall investigate especially the following questions: (1) the concentration of the double salt; (2) the degree of ionization of the double salt; (3) the velocity of migration of the ions of the double salt; and (4) the velocity of decomposition of the double salt and its ions.

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[1] A similar study involving the hydrogen electrode is now in progress in this laboratory.

EXPERIMENTAL.

On the Reaction of Iodacetonitrile with Silver Nitrate.

The methods previously described for making the iodacetonitrile did not seem to give sufficiently good yields, and it appeared advisable to try to improve them. The plan followed was that of Scholl and Steinkopf,[1] Bauer,[2] and Henry.[3] Ethyl chloracetate, boiling at 143°–146°, was made from Kahlbaum's chloracetic acid and ethyl alcohol in the presence of sulphuric acid. The chloracetamide was obtained in 90 per cent. yield by treating the ester with 3 volumes of a concentrated solution of ammonia which was saturated with ammonia gas at 0°. The crude chloracetonitrile was obtained in nearly 100 per cent. yield by mixing the chloracetamide with a molecular equivalent of phosphorus pentoxide and slowly distilling off the nitrile. The iodacetonitrile was made by boiling the chloracetonitrile in three volumes of pure methyl alcohol with five molecular equivalents of potassium iodide (instead of two equivalents used by Henry) under a return condenser 12 hours (instead of 5 hours, as recommended by Steinkopf). The excess of alcohol was distilled off and the residue was poured into several volumes of water, whereupon a dark brown heavy oil separated out. This iodacetonitrile was washed with a solution of sodium thiosulphate to remove the free iodine and was then dried with anhydrous sodium sulphate. It can be purified by distillation under diminished pressure, the boiling point being 65°–67° at a pressure of 4–6 mm. The iodacetonitrile did not at any time distil over, nor remain, colorless, as the other authors state. The color, after four purifications and fractionations, was a light yellowish green, which, however, did not increase in intensity even after the oil stood eight months. By extraction with ether, some of the iodacetonitrile can be recovered from the wash water.

The complex salt, $AgNO_3.ICH_2CN$, was prepared according

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[1] Ber. d. chem. Ges., **29**, 2417. Steinkopf: *Ibid.*, **41**, 2540. Braun: *Ibid.*, **41**, 2135.

[2] Ann. Chem. (Liebig), **229**, 167.

[3] Bull. soc. chim., **47**, 400.

to the method described by Scholl and Steinkopf by allowing the iodacetonitrile to flow from a separatory funnel into a solution of silver nitrate in water. A light yellow precipitate settled out immediately, which, when separated from the solution, dried, and recrystallized twice from water at 50°, melted at 121°.

The preliminary method chosen for studying the question whether appreciable quantities of the iodacetonitrile and silver nitrate form a double compound was, as stated above, the determination whether the conductivity of this mixture is different from that of a solution of silver nitrate having the same concentration. The concentration of the silver nitrate solutions varied from 0.1 N to 0.0025 N, and the values given are only approximately correct, as can be seen from the conductivity data. Since in each case, however, the same solution was used in the check experiments there is no doubt as to the validity of the conclusions. In each one of our preliminary experiments there was a precipitation of the complex salt or a formation of silver iodide. The conductivity was therefore lowered, as is shown in the following tables:

	μ.	Temp.
50 cc. 0.01 N $AgNO_3$ solution in water	63.52	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with ICH_2CN	57.20	0°
50 cc. 0.005 N $AgNO_3$ solution in water	120.93	25°
25 cc. 0.01 N $AgNO_3$ solution and 25 cc. water saturated with ICH_2CN	95.67	25°

In methyl alcohol the same general results were obtained; in this case the precipitate formed was apparently colloidal in nature and clouded the whole solution:

	μ.	Temp.
50 cc. 0.02 N $AgNO_3$ in CH_3OH	70.42	25°
25 cc. 0.04 N $AgNO_3$ and 25 cc. 0.04 N ICH_2CN	48.59	25°

The results obtained in ethyl alcohol and acetone were exactly analogous to those cited above. Owing to the small solubility of silver nitrate in acetone 0.001 N solutions were used. Other similar results were obtained, but will not be given here.

Since in all of these solvents there was rapid precipitation of the double salt or of silver iodide, we made some very careful attempts to free the iodacetonitrile from all hydroiodic acid or other substance that would conduct the current in water, or that would react quickly with silver nitrate. This was done by shaking the oil several times with solutions of dilute alkali, and sodium thiosulphate, and then with small volumes of conductivity water until the aqueous solution showed no appreciable conductivity above that of the water. In this way approximately 0.1 N aqueous solutions of iodacetonitrile can be obtained which give no precipitate with silver nitrate at 0° or at 25° before 30 minutes. The conductivity of such a mixture can be easily measured, and when this is done it is seen that the conductivity of the mixture of silver nitrate and iodacetonitrile is not measurably different from that of silver nitrate in the same concentration.

The water used in all of the following experiments had a conductivity of not more than 1.83×10^{-6}, and corrections are, of course, made for this. The saturated aqueous solution of iodacetonitrile had practically the same conductivity as the water used. For instance, 50 cc. of one solution had a conductivity 2.0×10^{-6}, while another had the conductivity 1.96×10^{-6}. In the following experiments there was no precipitate nor cloudy appearance visible in one hour after mixing the solution at 0°, nor in 20 minutes at 25°:

	μ.	Temp.
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. conductivity water	70.1	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with iodacetonitrile	69.98	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. conductivity water	125.1	25°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with iodacetonitrile	125.1	25°

Similar experiments were performed in absolute methyl alcohol, which had a conductivity 2.3×10^{-7}. No visible precipitate was formed in 4 hours:

	μ.	Temp.
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. methyl alcohol	81.2	25°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. 0.02 N iodacetonitrile in CH_3OH	80.79	25°

Entirely analogous results were obtained by dissolving the pure double compound in these solvents and measuring the conductivities.

The results of these experiments lead us to the conclusion that no appreciable amount of the double compound,

$$AgNO_3.ICH_2CN,$$

exists in a solution of a mixture of silver nitrate and iodacetonitrile, or of the double compound, in water, acetone, methyl alcohol or ethyl alcohol. These conclusions may not be final, and, as stated above, we shall use still other methods in studying this question. The rapid precipitation of the double compound, $AgNO_3.ICH_2CN$, from aqueous and alcoholic solutions of the components must be due, therefore, to the small solubility of this substance and not to its appreciable concentration at any moment.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, June 1, 1910.

THE TITRIMETRIC ESTIMATION OF PHOSPHORUS IN SMALL AMOUNTS.

BY L. T. BOWSER.

A number of different procedures have been advocated and used for the determination of phosphorus in very small amounts, some of them good and others indifferent, but each apparently with some defect. With but one exception, so far as the writer has been able to gather from the literature of the subject, all these methods are colorimetric, the one exception being described by Veitch[1] in a short paper on the titra-

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U. S. Bur. Chem., Bull. **90**, 188 (1904).

tion of small amounts. The objection to most of these colorimetric methods is the fact that any silica present in solution produces an effect similar to phosphorus, and on this account they are somewhat difficult of manipulation, and good results are by no means certain. A number of different investigations by the writer having shown the great accuracy and facility, under properly controlled conditions, of titration methods for the determination of small amounts of various other substances, it was thought that phosphorus should be capable of estimation by the same general procedure. With this in view, a short series of trials was carried out to see what would be the possibilities of such a method.

Veitch used for titrating the phosphomolybdate precipitate a standard hydroxide solution, one cc. of which was equal to 0.0005 gram P_2O_5. His results, while good as far as they went, were neither numerous enough nor obtained under sufficiently varied conditions to give definite conclusions for general work. His standard hydroxide solution was approximately N/6 in strength, and it seemed that by the use of a solution considerably more dilute very accurate results might easily be attained.

The first standard phosphorus solution used for these tests contained 1 milligram PO_4 per cc., or 1000 parts per million. Ten cc. of this solution was diluted up to one liter, so that 1 cc. contained 0.01 mg. PO_4, or 0.007474 mg. P_2O_5. Different volumes of this solution were taken so as to have present the desired amounts of phosphoric acid and in each case were evaporated to a volume of about 5 cc. before precipitating. To each was added about 0.2 gram of ammonium nitrate and 3 cc. molybdate solution. The standard alkali used was prepared from one regularly in use, and equivalent to 0.000179 gram P_2O_5 in 1 cc., by diluting 170 cc. up to 500 cc. Of this solution 1 cc. is equivalent to 0.00006086 gram P_2O_5. The phosphorus solutions were precipitated at 55°, kept at that temperature for one hour on the water bath, allowed to stand for two hours at room temperature, then filtered on a small asbestos pad about $^1/_{16}$ inch thick and washed with the usual wash solution containing potassium nitrate.

All titrations were carried out in exactly the same way as with larger amounts. The results of the first set are given in Table I:

Table I.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	10	0.07474	1.15	0.06999	—0.00475		
2	10	0.07474	1.35	0.08216	0.00742	0.00133	1.78
3	20	0.1495	2.30	0.1400	—0.00950		
4	20	0.1495	3.10	0.1887	0.3920	0.0148	9.90
5	30	0.2242	4.50	0.2739	0.0497		
6	30	0.2292	4.35	0.2587	0.0345	0.0421	1.78
7	40	0.2989	5.35	0.3256	0.0265		
8	40	0.2989	5.45	0.3317	0.0326	0.0295	9.87
9	50	0.3737	7.15	0.4473	0.0736	0.0736	19.70
10	50	0.3737	lost	....	....	....	...
11	100	0.7474	13.40	0.8155	0.0681		
12	100	0.7474	14.00	0.8521	0.1047	0.0864	11.56

After completing the titrations of this set a blank run was made on the asbestos used, although it had not been suspected that any error from this source was probable. However, four titrations required respectively 0.5, 0.45, 0.45, and 0.5 cc. potassium hydroxide, hence 0.5 cc. was subtracted from each titration result, giving the volumes noted in Table I, and bringing the results to a much more reasonable average than they at first appeared. Even with this correction, however, none of the results are good enough to show the capabilities of the method, on account of the decided irregularities that occur.

Another standard phosphate solution was now made up from C. P. microcosmic salt, with an approximate strength of about 0.1 mg. P_2O_5 per cc. of solution. When a determination of the actual strength was made, using for purposes of titration an accurately standardized caustic potash solution, 1 cc. of which was equivalent to 0.56 mg. P_2O_5, it was found necessary in every case to use 9.6 cc. of the alkali to dissolve the precipitate from 50 cc. of phosphate solution, thus showing a strength of 0.1075 mg. P_2O_5 for 1 cc. of the standard phosphate solution. Some trouble having been experienced, in a series not here recorded, with the settling down of molybdic acid in crystals, giving results entirely inaccurate, it was thought that perhaps too much molybdate solution had been used, hence a calculation, based on the amounts used in the "Official Methods," was made to learn the proper volume for use. It was found that 0.5 gram ammonium nitrate should be taken, and for 1 mg. P_2O_5 about 1.5 cc. molybdate, or 1 cc. for quantities less than 0.8 mg. For the second set, shown in Table II, the new phosphate solution was used, evaporated down as in the first set, and the phosphorus precipitated with the amounts of reagents just noted. Each was made up to a volume of approximately 10 cc. before precipitation in order to insure uniformity of conditions:

Table II.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	1	0.1075	2.45	0.1491	0.0416		
2	1	0.1075	2.65	0.1613	0.0538	0.0477	44.37
3	2	0.2150	3.85	0.2343	0.0193		
4	2	0.2150	3.95	0.2404	0.254	0.0233	10.37
5	3	0.3225	5.40	0.3286	0.0061		
6	3	0.3225	5.60	0.3408	0.0183	0.0122	3.78
7	4	0.4300	7.00	0.4260	—0.0040		
8	4	0.4300	7.10	0.4321	0.0021	—0.0010	—0.23
9	5	0.5375	10.15	0.6177	0.0802		
10	5	0.5375	9.45	0.5751	0.0376	0.0589	10.96
11	10	1.0750	18.05	1.0990	0.0240		
12	10	1.0750	17.85	1.0860	0.0110	0.0175	1.63

This set, too, exhibits considerable irregularity and cannot be considered as satisfactory, although several of the determinations are so. In order to ascertain as to whether the trouble could be attributed to the separation of molybdic acid, four blank tests were made, using 10 cc. of water and proceeding as usual. Decided amounts of the acid settled on the bottom of the beakers and wherever the stirring rods had been moved. Two of these required respectively 2.05 and 3.30 cc. of standard caustic potash (while from appearances the other two would have required even more), hence it seemed certain that here was where the trouble arose. Four more blank tests were then made, using in this instance 20 cc. of water and proceeding as usual. After deducting the correction for the asbestos it was found that no molybdic acid had settled in any of these, showing that the volume of solution when ready for precipitation should be not less than 20 cc. After thus locating the cause of difficulty another set was run which was in every way a duplicate of Set II, save that each solution was diluted up to about 20 cc. before precipitation. Following are the results, the correction for the asbestos having been 0.25 cc. in this case:

Table III.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	1	0.1075	1.90	0.1156	0.0081		
2	1	0.1075	2.20	0.1339	0.0264	0.0172	16.00
3	2	0.2150	3.95	0.2404	0.0254		
4	2	0.2150	4.10	0.2496	0.0346	0.0300	13.95
5	3	0.3225	5.80	0.3530	0.0305		
6	3	0.3225	5.50	0.3347	0.0122	0.0213	6.61
7	4	0.4300	7.30	0.4443	0.0143		
8	4	0.4300	7.05	0.4291	0.0009	0.0067	1.56
9	5	0.5375	8.75	0.5325	—0.0050		
10	5	0.5375	8.85	0.5386	0.0011	—0.0020	—0.37
11	10	1.0750	17.10	1.0410	—0.0340		
12	10	1.0750	17.15	1.0440	—0.0310	—0.0325	—3.02

These results were thought to be accurate enough for such work as is usually encountered; in fact it is doubtful if any better ones could be secured by any method, so attention was turned to its application in actual work. For this purpose a sample of floats was taken, containing silica, iron, aluminium and many other substances, in addition to phosphorus. One gram of floats was treated with nitric acid in the usual way to dissolve out the phosphorus, and the filtrate was made up to a liter, of which aliquot parts were taken up for the determinations. To 500 cc. of this solution was added 1.2014 grams of water glass, in order to make certain of having a fair amount of silica present, since tests on the original solution had failed to show the presence of any appreciable amount. Four aliquot parts of each solution were taken, each containing 25 cc., and the phosphoric acid determined by the usual volumetric method. One cc. of the potassium hydroxide solution used was equivalent to 0.00056 gram P_2O_5. Results were as follows:

Table IV.

No. 1 (without silica).		No. 2 (with silica).	
KOH. cc.	P_2O_5. Per cent.	KOH. cc.	P_2O_5. Per cent.
16.70	37.32	16.60	37.18
16.60	37.18	16.25	36.40
16.65	37.30	16.30	36.51
16.70	37.32	16.35	36.62
Average,	37.28	Average,	36.74

It will be seen that slightly higher results were obtained when silica was absent than when it was present. A 25 cc. portion of each solution was now diluted up to 250 cc. for estimation of the phosphoric acid by the proposed method. Four 20 cc. aliquot parts of each solution were taken, and the precipitation, washing, and titration carried out as in Set III, the results being as follows:

Table V.

Without silica.				With silica.			
No.	KOH. cc.	P_2O_5. mg.	Per cent. or parts per million.	No.	KOH. cc.	P_2O_5. mg.	Per cent. or parts per million.
1	11.95	0.7273	37.49	5	12.90	0.7851	39.25
2	12.30	0.7486	36.36	6	12.20	0.7425	37.12
3	11.95	0.7273	37.43	7	12.15	0.7395	36.97
4	12.15	0.7395	36.97	8	12.00	0.7303	36.52
		Average,	36.78			Average,	36.87[1]

These results are certainly quite satisfactory, and agree very closely with the values found by the regular volumetric method. Silica, it seems, does not appreciably influence the results, contrary to its behavior in the colorimetric methods and to the generally prevailing impression. The filtrates

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[1] Omitting No. 5.

from the portions containing silica were of far greater color intensity than the others, having a deep yellow tint, but the precipitates were identical in appearance. It seems probable that the silicomolybdates formed at the same time as the phosphomolybdates are not precipitated, but remain in solution and are filtered off, hence if a proper excess of molybdate solution be present initially no trouble should be experienced by reason of the presence of silica.

It was now determined to take a still more dilute phosphorus solution and add more silica, to see if a large excess of the latter would really interfere. For this purpose an 83.33 cc. portion of each of the preceding solutions was diluted to 250 cc., thus making it just one-third as strong as before. To the one already containing silica was added 1.6367 grams more of water glass, making a total of 1.8369 grams in the 250 cc., as against 0.00833 gram of sample, and 20 cc. portions were used for precipitation. No flattering success marked this attempt, but the results may be instructive nevertheless. In the solution where silica was present the larger portion was immediately precipitated by the free nitric acid of the molybdate reagent, forming a gelatinous mass, which promptly clogged the filter and rendered subsequent filtration and washing excessively slow. Only two of these precipitates were filtered, requiring about two hours for each. Results were as follows:

Table VI.

	No. 1 (without silica).		No. 2 (with silica).	
	KOH. cc.	Parts per million.	KOH. cc.	Parts per million.
	3.55	10.80	4.15	12.63
	4.15	12.63	3.80	11.56
	3.75	11.41		
	4.25	12.93		
Average,		11.94		12.09
or		35.82 per cent.		36.27 per cent.

It is evident that the best conditions had been overstepped here, and that too small an amount of phosphoric acid was present, but, as before, it seems that silica did not affect the final results, hence no great caution in guarding against it is needed. From the standpoint of general utility it is believed this method will be found valuable, and it is hoped it may prove as useful to others as it has to the writer.

Briefly stated, the method is as follows: Use a convenient volume of solution, but see that when ready for precipitation it is not less than 20 cc. For less than 0.8 mg. P_2O_5 use 1 cc. molybdate solution, for more 1.5 cc. and 0.5 gram ammonium nitrate, precipitate at 55°, keep for one hour at that temperature, let stand for two hours, filter and wash. Titrate with a standard hydroxide solution not stronger than 0.02 N.

105 Grove St.,
LYNN, MASS.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

BY H. N. MORSE, W. W. HOLLAND AND J. L. CARPENTER.

PART II. THE MANOMETERS.

After the cells and the membranes had been perfected to such an extent that the solutions within could be relied upon to maintain their maximum pressures for weeks together, and to exhibit their original rotation when taken out, the problem of manometers assumed an altogether new importance; for they then became almost the sole measure of the possible further refinement of the work. With sufficiently accurate manometers at hand, there was no obvious reason why osmotic pressure should not be measured with a precision which would compare favorably with the best quantitative work in other fields. It was the conviction that, thenceforward, the principal problem was the improvement of these instruments which led the authors to devote over ten months to the preparation and verification of the manometers which were used in their latest attempt to determine the temperature coefficient of osmotic pressure. They are obliged to con-

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[1] The work upon osmotic pressure which has been in progress in this laboratory during the past 10 years is aided by grants from the Carnegie Institution. The earlier papers will be found in THIS JOURNAL, **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257; **45**, 91.

fess, however, that they are not wholly satisfied with the result. The reasons for this dissatisfaction will appear in connection with the various steps in the preparation of the instruments, likewise the remedies which it is proposed to employ in future work.

To those who have had experience with manometers of very small bore, it is well known that the material which ordinarily passes for pure mercury in the laboratory is by no means suitable for manometric work, and that to obtain it in adequately pure condition for this purpose, one must take much more than the usual pains with its purification. The mercury used in our manometers—and also that which is now used in the bath thermostats—is cleansed in the following manner:

1. The commercial material is first filtered through paper filled with pinholes, to free it from dirt. It is then heated for four hours to the boiling point in a glass flask with a very long neck for the condensation of the vapors; and during this time a current of air is forced through the hot metal. On cooling, it is again filtered to remove the scum which usually forms in considerable quantity.

2. It is distilled in a vacuum.

3. The distillate is washed by the method of Lothar Meyer, but with water containing two per cent. of nitric acid and two per cent. of mercurous nitrate instead of a solution of ferric chloride. The apparatus in which the washing is done consists of a wide glass tube, two meters in length, to the lower end of which is fused a quite narrow tube of the usual double U form, the proportions of the descending and ascending limbs being so selected that the mercury which is used to support the cleansing liquid shall lie wholly within the smaller tube. To admit the mercury at the top and to regulate the flow, a separating funnel is employed, the lower end of which has been widened out into the form of an inverted funnel. Over this are tied two or three thicknesses of the finest silk bolting cloth. The material to be purified is thus made to enter the cleansing liquid in hundreds, and perhaps thousands, of excessively fine streams. It is passed *1000 times* through the solution of nitric acid and mercurous nitrate.

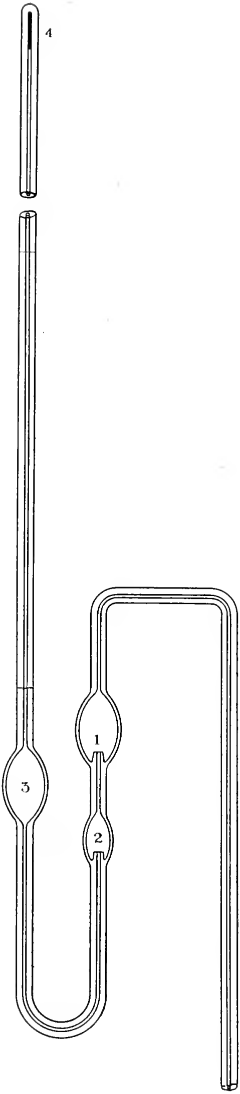

Fig. I.

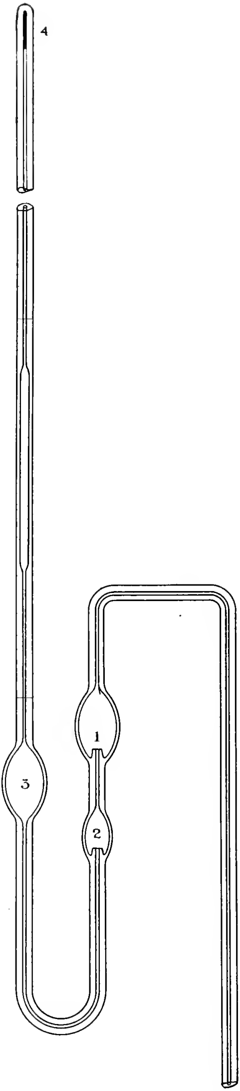

Fig. II.

4. After treating the mercury as described under (1), (2) and (3), it is washed with water, dried, and again distilled in a vacuum, but in a still which is used for no other purpose, *i. e.*, not in the still (2) which is used for the first distillation. The mercury which has been thus cleansed retains its brilliant luster in the air, and its movements in narrow tubes are highly satisfactory. We have also prepared the mercury for manometers from the purest oxide which we could make, but have not found the product superior in any way to mercury which has been purified as described above.

A paper[1] on the manometers then in use was published in 1908. But the practices of that time were modified so radically, in preparing for the recent work, that an entirely new presentation of the subject appears to be called for.

The form of the instruments which have been used in all the measurements to be presented in this series of papers is seen in Fig. I. The bore of these manometers varies from 0.45 mm., in the narrowest one, to 0.72 mm. in the widest one. The principal reasons for using tubes of very small internal diameters are:

1. In wide tubes, the short mercury columns (4,Figs. I and II) which fill the upper ends of the manometers are often dislodged by the severe tapping to which the instruments are subjected at certain times.

2. The compression of the small volume of gas which they contain involves but little dilution of the solution in the cell.

3. Relatively small volumes of mercury are required by manometers of small bore.

The disadvantages are:

1. It is more difficult to deal satisfactorily with the meniscus in a narrow tube.

2. The capillary depression is large in small tubes, and it varies so greatly with slight irregularities of bore that it is practically impossible to know exactly what correction is to be applied, except at those points in a tube where the capillary depression has been determined experimentally.

3. The movements of the mercury in small tubes are greatly

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[1] THIS JOURNAL, **40**, 325.

influenced by minute quantities of impurities, whether the same are dissolved in the metal itself or are attached to the surface of the glass.

Fig. II shows a form of manometer which has some distinct advantages over that seen in Fig. I. The volume of the nitrogen in such an instrument is relatively very large, a length of 1 mm. in the wider portion of the tube being about equal in capacity to a length of 16 mm. in the narrower part. The column of mercury which occupies the upper end is in the narrower part of the tube and is, therefore, not easily dislodged by tapping. In this respect, instrument No. II is not inferior to No. I. During a measurement of pressure by No. II, the whole of the nitrogen is compressed into the upper and narrower part of the manometer, hence the column of the gas is much longer for any given pressure than in No. I—so much longer, in fact, that unavoidable errors of meniscus and capillary depression become quite unimportant. In this respect No. II is greatly superior to No. I.

Manometers like that shown in Fig. II are designed more especially for the measurement of the pressure of concentrated solutions, where errors of meniscus tell heavily on the results unless large volumes of gas are used. In the case of dilute solutions, large gas volumes are obviously less necessary as a means of minimizing such errors.

The length of the wider portion of the second form of manometer is varied according to the pressure which it is desired to measure, *e. g.*, if the pressure in question is between 4 and 6 atmospheres, the wide and narrow parts are so related that the mercury meniscus will appear in the latter at some pressure slightly below 4 atmospheres. In instruments designed for use with normal solutions, on the other hand, the nitrogen is not all compressed into the narrower portion of the tube until a pressure of more than 20 atmospheres is reached.

No considerable increase in the dilution of the solution results from the larger volume of gas in such manometers, because, at the time of closing the cell, a mechanical pressure is brought to bear on the contents which is nearly equal to the osmotic pressure. Hence the subsequent diminution in the volume of the gas is small.

We have found the form of manometer represented in Fig. II much superior to that shown in Fig. I, but it is to be distinctly understood that the latter only has been used in the recent attempt to determine the temperature coefficient of osmotic pressure. Having once begun the work with the older style of instrument, it was thought that, whatever might be its faults, the errors resulting therefrom should affect all the measurements alike, rather than only a portion of them.

It will be noticed that two of the manometer bulbs are provided with "traps," 1 and 2, Figs. I and II. By means of these the mercury is made to enter the narrow tubes below at points somewhat above the bottom of the bulbs. The purpose of the arrangement will be understood from the following explanation: When the solution in the cell is under pressure, it enters to some extent the upper end of the nearest bulb (1), and when the pressure is afterwards removed and the mercury which had been previously expelled returns, it is apt to entangle minute drops of the solution between itself and the wall of the bulb. Occasionally one or more of these will persistently work its way forward towards the calibrated end of the manometer, making it necessary, sooner or later, to open, cleanse, and refill the instrument. The "traps" are an effectual preventive of such calamities. Before their introduction, it was necessary frequently to inspect the manometer for the presence of these migrating particles of liquid, and it happened, at times, that, notwithstanding the greatest vigilance, they escaped detection until it was discovered that the manometers were no longer measuring correctly.

The third bulb, 3, Figs. I and II, prevents the possible escape of nitrogen from the calibrated portion of the manometer. As stated already, the solution in the cell enters the upper end of bulb No. 1; and, before the instrument can be used for another measurement, it is necessary to remove the liquid which has thus made its way from the cell into the manometer, and, after washing the glass, to replace it either with mercury or with the solution whose pressure is to be measured. These operations involve a considerable diminution of the pressure on the nitrogen, and the purpose of the bulb (3) is to serve at such times as a safe reservoir for the expanded gas.

There are two very fine marks etched upon each manometer, one at or near the lower end of the calibrated portion of the instrument, and the other higher up. All data, whether they pertain to calibration or the measurement of pressure, are referred to one or the other of these marks. Two are made, because one of them is often out of sight in the bath, in which case the readings can be referred to the other. The exact distance between the two marks is known, hence readings which have been referred to one are readily translated into terms of the other. No graduation of manometers is attempted, because even the finest lines upon the glass interfere with the accurate location of the meniscus.

The short columns of mercury at the upper ends of the manometers, 4, Figs. I and II, serve to prevent contamination of the nitrogen while the instruments are being closed, and to keep the gas afterwards out of that portion of the tubes whose calibration has been affected to an unknown extent by fusing off the ends.

Fig. III represents an instrument which is in very frequent use in connection with the manometers. The manner of its use will be best illustrated by describing some of the operations in which it is most frequently employed:

1. Suppose the whole instrument, except the space occupied by the nitrogen, is filled with mercury, and it is necessary to cut off the tube between the bulbs 1 and 2, either for the purpose of replacing the detached piece by another of similar form, or by a simpler piece of glass tubing. The rubber-covered cone upon the open end of the manometer, or a sharply sloping stopper through which the end has been passed, is placed in the cup 1 (Fig. III). The air is then exhausted through a rubber tube attached to the stem at 2. When a sufficient quantity of mercury has been drawn into the cup, the whole arrangement is tipped backward until the

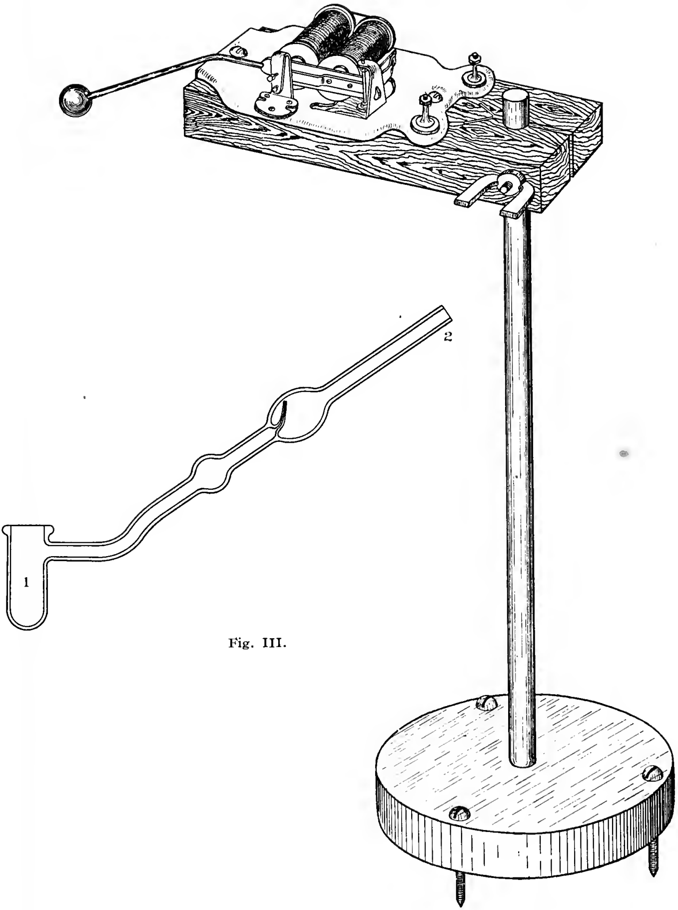

Fig. III.

Fig. IV.

end of the manometer is exposed. Air is then cautiously readmitted to fill the space in the instrument which was previously occupied by the mercury.

2. Suppose the open end of the manometer, *e. g.*, to the middle of bulb No. 1, is filled with air and it is desired to replace it with mercury. A quantity of mercury is poured into the bottom of the cup, the manometer is inserted, and with the open end exposed, the air is exhausted, as before, through the rubber tube. On bringing the manometer again to the upright position so as to immerse the open end, and readmitting air, the mercury flows into the tube to replace the air which has been withdrawn.

3. Suppose, again, the manometer has been used in a measurement of pressure, and the open end—perhaps also a small portion of bulb No. 1—is filled with the solution. Before the instrument can be used in another experiment, this must be replaced, either by mercury or by some of the solution whose pressure is to be determined. The necessary manipulation will be readily understood from what has already been said. The course of procedure in the second case is as follows: (1) The solution is removed and replaced by air; (2) the air is replaced by the new solution, and this is, in turn, replaced by another portion of the same solution, etc., until there is no danger that the concentration of the new solution will be affected by the older one. If mercury is to be substituted for a solution, the tube must be washed and dried before introducing it. In this case portions of the wash liquids—water, alcohol and redistilled ether—are introduced and removed exactly in the same manner as when one solution is to be replaced by another. The final drying of the manometer is accomplished by attaching a tube containing a drying agent to the stem (2) and alternately exhausting and readmitting air.

Another important instrument is the "tapper" shown in Fig. IV. In a measurement, the mercury in the manometers has time enough to adjust itself to any pressure, but in operations connected with the calibration, comparison, and verification of these instruments, the "lag" of the mercury must be overcome by jarring the tubes, and frequently the tapping to which it is necessary to subject tubes of small bore is severe and prolonged. This is notably the case in manometers in which the glass is not perfectly clean, or has been slightly roughened by the reagents employed in cleansing it.

The construction of the "tapper" is so obvious that it is only necessary to notice two or three of its features. It is strongly inclined, when in operation, to move away from the tube which the "hammer" is striking. Hence the base is made of lead, for the sake of the greater weight, and is mounted upon three very sharp-pointed steel pegs which sink somewhat into the wood on which the instrument rests. The "hammer" is covered with rubber or leather to prevent the possible shattering effects of its blows. In the "*manometer house*," where all operations requiring a constant temperature and the use of the cathetometer are carried out, there are five of these instruments, each one of which is connected by means of a flexible wire cord with a hand push-button located at the cathetometer, so that the operator can tap any tube within the house without removing his eyes from the telescope.

The steel instrument seen in Fig. V is employed in determining capillary depression, in the calibration of manometers, in the determination of nitrogen volumes, and in the comparison of the manometers with one another or with a standard instrument. It is known—and for convenience will be referred to hereafter—as the "*steel block*." An instrument identical with it—except that it contained two places for manometers instead of three—has been described in a former paper.[1] The main feature of the block and the purpose of the various parts will be apparent on an inspection of the figure. It contains a reservoir (1) which is filled with mercury, and two plungers, one (2) large and the other (3) small. The larger one is employed for the coarser, and the smaller one for the finer, adjustments of pressure in the glass tubes 4, 5 and 6. The packing (7, 8, 9, 10 and 11), which

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[1] This Journal, **40**, 328.

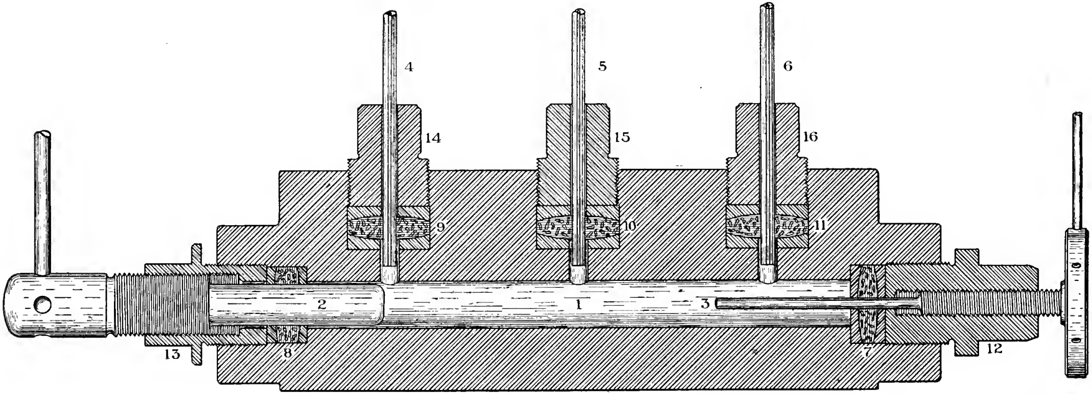


Fig. V.

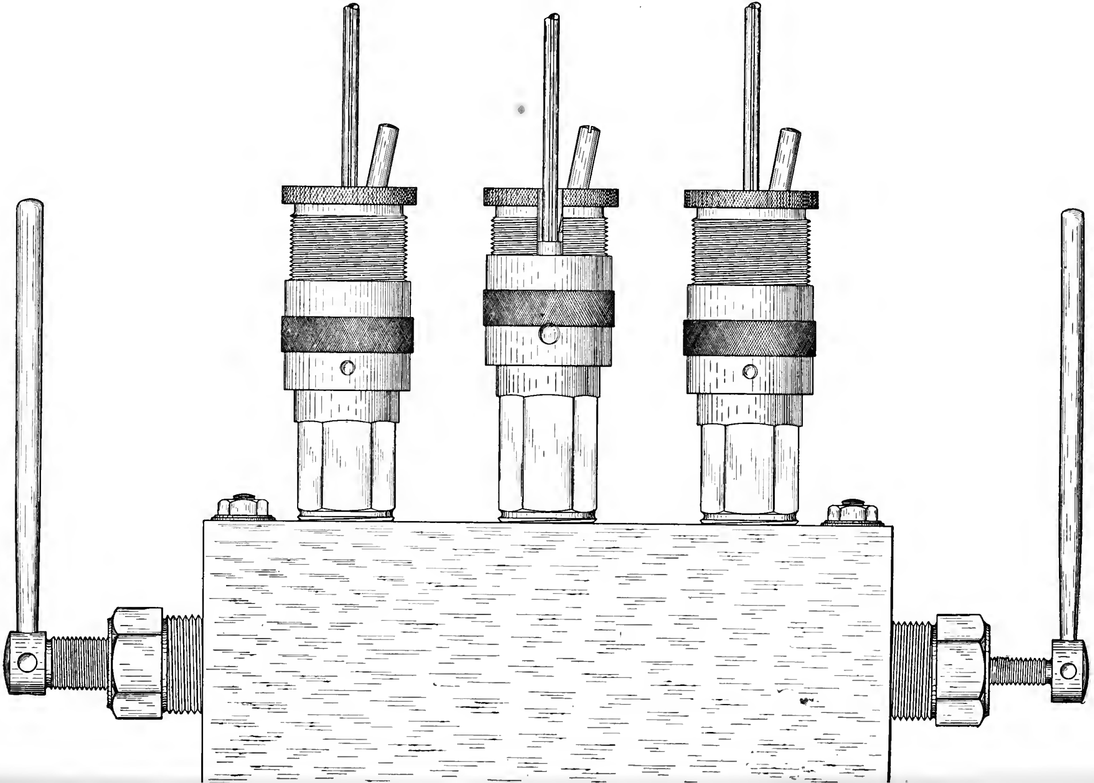
may be of leather or rubber, or partly of both, is held, in each case, between the concave surfaces of two steel discs, and the required pressure is brought upon these by means of the threaded plugs 12, 13, 14, 15 and 16. The instrument has been tested and found to be *mercury-tight* up to 300 atmospheres.

Pure mercury only is put into the block, but it cannot be presumed, under the prevailing conditions, to maintain its purity; hence some precautions are necessary to prevent a possible contamination of the mercury in the manometers, or a fouling of the glass walls of the tubes near the open ends. The usual precaution, when a manometer is to be placed in the block, is to cut off the end (between the two bulbs, 1 and 2, Figs. I and II) and to replace the detached piece by another of suitable form and capacity, which is afterwards filled with pure mercury. When the manometer is taken from the block, the piece previously detached is restored to its place. A simpler way is to leave the manometer uncut and, after its removal from the block to draw out a large portion of the mercury and replace it with fresh mercury. This, however, involves the risk of fouling the tube and the necessity of cutting off the end afterwards for cleansing purposes.

The principal objection to the block is that, owing to the large mass of metal in it, its changes of temperature are very slow, and that, on this account, it is necessary to maintain a very constant temperature in the "manometer house" in which the block is located. It will be seen that with falling temperature in the block, however slight, a meniscus in a manometer which is under observation must always tend to take on a flattened or even a concave form, while, with rapidly changing temperature, whether upwards or downwards, a meniscus in the manometer cannot maintain a fixed position for any length of time. The obvious remedy is the maintenance of a perfectly constant temperature in the block, and this we attempt to accomplish by blowing over the instrument, day and night without cessation, a current of air of nearly constant temperature. The same difficulty is experienced, though in a lesser degree, with instruments of smaller mass.

Whenever occasion arises for a redetermination of the nitrogen volume of a manometer which has been used in the measurement of pressure, it is necessary, before placing it in the steel block, to remove the brass cone by means of which the manometer is fastened in the cell. Instead of melting the Wood's metal and separating the cone from the glass, it is customary to cut off a piece of the tube with the cone attached and to fuse on in its place for temporary use another piece of glass tubing. In this way a resetting of the cone is avoided. But, since the redetermination of the nitrogen volumes and the comparison of manometers in use are constantly recurring operations, much time and trouble are saved by using the "*brass block*" shown in Fig. VI. The internal arrangements of this instrument are precisely the same as in the steel block, except in the upper part where the manometers are inserted. There we have exactly reproduced in brass all the parts which are concerned in the closing of any cell after the manometer has been introduced. As a whole, the arrangement is, therefore, to be regarded as consisting of three brass cells, all communicating with a common reservoir, with facilities for bringing to bear on the liquid within any desired pressure. The manipulation involved in placing a manometer in the brass block is identical with that of closing a cell, and it is not necessary to remove the cone. The liquid used in the reservoir is either water or an aqueous solution of the substance whose osmotic pressure is being studied. One advantage of the brass over the steel block is that in it we have more nearly reproduced the conditions under which osmotic pressure is measured by the manometer, the principal difference being that the pressure exerted upon the nitrogen is mechanical instead of osmotic. It may be of passing interest to mention that the brass block, weighing about 25 kilograms, was made wholly from apparatus which was designed and found to be inadequate during the unsuccessful attempt to form the finished cell under pressure.

Fig. VII shows the arrangement of the "manometer house,"



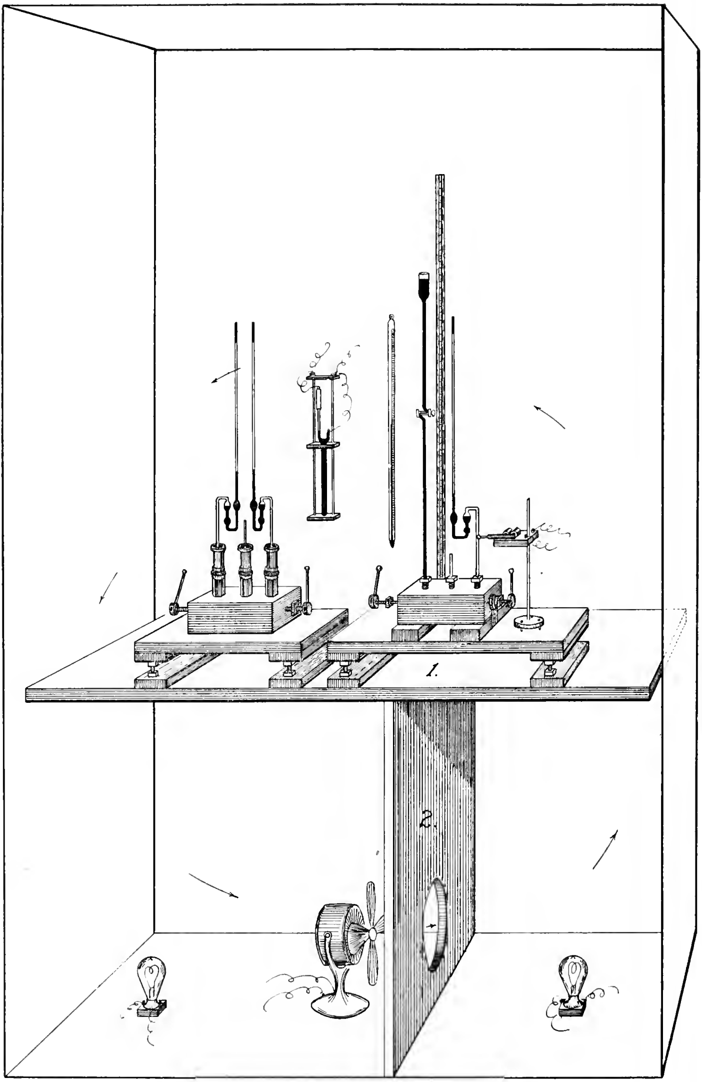


Fig. VII.

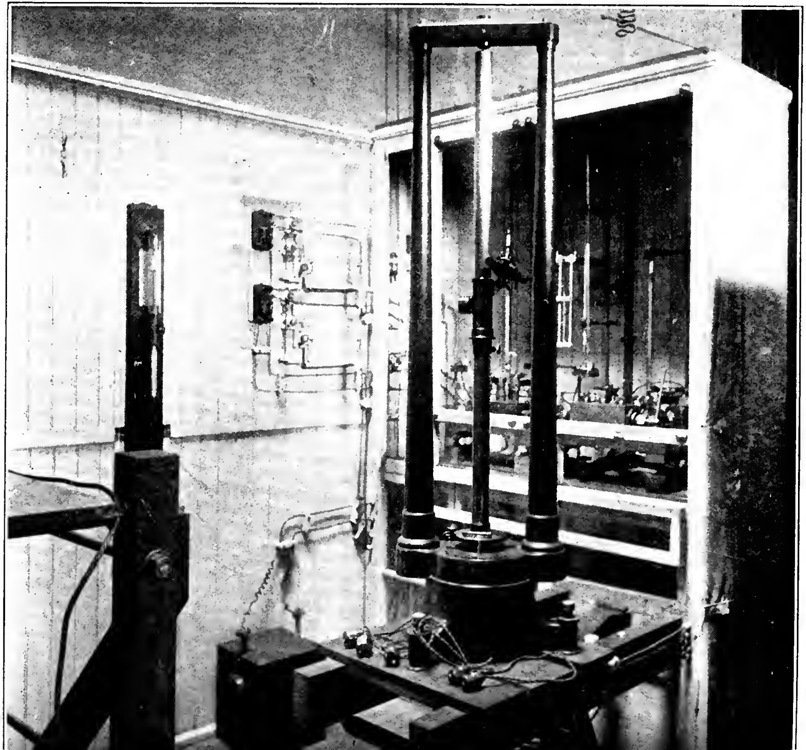
in which a constant temperature is maintained, and where all experiments on manometers, except calibration in the horizontal position, are carried out. It contains the "steel block," the "brass block," the "tappers," a meter scale, a thermostat for the regulation of temperature, electric heaters, and a fan motor, all of which will be recognized in the figure. The shelf 1, on which rest the various instruments, is supported by heavy brackets (not shown in the figure) which are bolted to the heavy masonry wall behind and afford a perfectly satisfactory degree of stability for the instruments. At each end of the shelf, a space 5 cm. wide is left for the passage of air. Lamps are employed as a source of heat for the reason that they heat up and cool down more quickly than other electric heating appliances. They are under the control of the thermostat seen in the upper part of the house. The fan is stationed before a hole of equal diameter in the partition 2. By means of it, the air, heated by the lamps, is kept in continuous circulation over all the instruments in the house. The temperature which is maintained in the compartment is always higher by a few degrees than the highest temperature in the room in which it is located.

The remaining features are better shown by the photograph, Fig. VIII, where the manometer house is represented with the plate glass front removed. The end to the right and the top of the house are also of glass, though the latter is usually covered with a thick woolen pad and the former with a flannel curtain. The front is also provided with a flannel curtain (not seen in the figure). The frame for the glass at the top is removable, to provide for the extension of the house upwards when very long tubes are to be accommodated. The various windows and doors are made to close tightly against rubber cushions, or the cracks between them and the framework are covered with surgeons' tape. The tubes through which the wires pass into the house are, however, left more or less open to provide for ventilation.

The type of cathetometer used in all our measurements is seen in Fig. VIII. Three such instruments are in use, one for each of the three large baths in which osmotic pressure is measured. The cathetometer here shown is also used in connection with a high temperature bath which is located on the right, but is not within view. Near the base of the cathetometer are the five hand push-buttons, by means of which the observer at the telescope controls the tappers within the house. Under the cathetometer is seen a specimen of the kind of foundation which supports all the baths and instruments concerned in the measurement of pressure. It consists of heavy wooden brackets. One end of the horizontal timbers is buried in the thick brick wall behind the house, while the descending timbers pass through the floor and enter the same wall in the room below. Two such brackets are required for a cathetometer and three for a bath.

The tubes which are used in making manometers are the most nearly perfect for the purpose which it is possible for us to obtain. The essential requirements are that any tube shall be of very nearly uniform diameter throughout, and that the form of the bore in every part shall be circular. Very few, if any, tubes conform perfectly to both conditions. Our tubes are imported in lots of several kilograms, and those who select them abroad are urged to spare no pains in procuring material of the highest possible excellence. In each lot of selected material thus obtained, we usually find—though not always—a few tubes which answer all reasonable requirements.

The first step in making a manometer is to etch upon the tube the two fine lines previously referred to as lines of reference ("upper scratch" and "lower scratch"). These are made no coarser than is absolutely necessary in order that they may be distinctly seen with the telescope, since a meniscus behind any line, however fine, is apt, in a small tube, to give the observer trouble. One of the lines is placed as near to one of the ends of the tube as an ample allowance of glass for subsequent operations will permit, and this becomes the "*upper scratch.*" The distance from it of the second line, the "*lower scratch,*" depends upon the length which the manometer is to have—ultimately, of course, upon the height of the available space in the baths. The calibration is begun at the lower scratch and is continued somewhat above the upper one. On



the tube, below the lower scratch, and also on the end of the tube nearest it, is etched some common device for the purpose of identification. The tube is then cut between the two, leaving below the device, upon the part which is to be calibrated, enough glass for later operations. The detached end, having upon it the same device as the manometer, is carefully preserved. It was formerly used as a "*side tube*" whenever the volume of nitrogen in the manometer was to be determined or verified, also to settle at any time any doubts which might arise regarding the meniscus or capillary depression.

Near each end of the tube to be calibrated a small bulb is blown, which serves in case of accident to catch and save the threads of mercury which are used in calibrating the instrument in the horizontal position.

The next step is to determine the capillary depression at a number of places in the tube, all of which are located by reference to one of the scratches. In this operation the steel block is employed, and the side tube is either a very wide one or one whose capillary depression is already accurately known. The depression of the mercury in our narrowest manometer amounts to nearly 18 mm., *i. e.*, to more than 0.023 atmosphere. In those of medium bore, the depression amounts to very nearly 0.02 atmosphere In a carefully selected tube, the variation in capillary depression is not found to be sufficient to affect materially the measurement of pressure in concentrated solutions; but in the case of dilute solutions, it may amount to a sensible proportion of the magnitude measured. In the course of a calibration, we find the *mean* diameter of the whole tube, and we can, of course, at any time, calculate the *mean* diameter of short portions of it by means of the known weight and the observed and recorded lengths of the calibrating threads; but we are not able to deduce from the data thus far accumulated any safe rule by which the variations of capillary depressions in a tube can be derived from what is known or discoverable about the variations in the diameter of its bore. In other words, since it is not practicable to determine experimentally the capillary depression at every point in a tube, a part of the corrections which we apply for it may be to some extent erroneous. The error cannot, however, in any case, amount to a large proportion of the whole correction.

One method of calibration has been described in a former paper,[1] a brief outline of which will suffice for present purposes, since we shall probably abandon some of its features in future work. The manometer tube is placed in the steel block and nearly filled with mercury by advancing one of the plungers into the reservoir. A short thread of mercury is then introduced at the top, but so as to leave a cushion of air between it and the column of mercury below. The thread is lowered by manipulating one of the plungers until the bottom of the lower meniscus is opposite the lower scratch at which the calibration is to begin. In this position its length is determined. It is then raised until the bottom of the lower meniscus occupies the previous position of the top of the upper meniscus, when the length of the thread is again determined. The process of setting the thread end to end and of determining its length in each position is continued until the whole of the space which it is intended to calibrate has been covered. This done, the thread is run out of the tube and weighed. Afterwards, a thread of mercury filling the whole of the calibrated portion of the tube is introduced. Its length in the tube and also its weight are determined as in the case of the short thread. From the length and weight of the long thread. the mean diameter of the bore is calculated, and from the observations on the length of the short thread in the different parts of the tube, a calibration curve is constructed. Finally, a mean value for the meniscus is obtained from the length and weight relations of the short and long threads. It is clear that if we multiply the weight of the short thread by the number of times its length is contained in that of the longer thread, *i. e.*, by the number of times it was set end to end, the product will not be equal to the weight of the latter, and that the difference is the weight of the mercury which would be required to fill all the meniscus spaces which were left vacant in setting the short thread end to end up the tube.

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[1] THIS JOURNAL, **40**, 325.

Converting this difference in weight into volume, and dividing by the number of settings less one, we obtain a mean correction for a double meniscus, which is the meniscus correction to be applied in all our measurements of pressure, since the nitrogen in the manometers is always included between two mercury columns. This method of calibration is described in greater detail in the paper referred to above. It has been in less frequent use of late, principally because it requires the coöperation of two individuals and is less expeditious than the plan which has superseded it. The present mode of calibration differs from the older one only in the position of the tube during calibration and in the mode of shifting the threads. Instead of setting up the tube vertically in the steel block, it is placed in the horizontal position over a ruled mirror on the dividing engine. All the other features of the earlier method are retained, *i. e.*, the system of short and long threads, of setting the latter end to end, of finding a mean correction for the meniscus, etc. The manometers used in the present investigation were doubly calibrated, first in the vertical and then in the horizontal position. It is hardly necessary to mention the fact that the change in the mode of calibrating was preceded by a somewhat detailed comparison of the screw of the dividing engine with the graduation upon the meter scale.

Some innovations are necessary when a manometer of the form shown in Fig. II is calibrated. The narrower portions—below, from the lower scratch to the bottom of the wider part, and above, from the top of the wide part to the end of the tube—are calibrated with the same short threads, and the meniscus correction is obtained from the length and weight of a single long thread which fills the upper narrower portion of the tube. So far the method does not differ from that already described. It remains, however, to ascertain the capacity of the wider part as a whole, and eventually in terms of the calibration unit. To do this, the wider part is slightly more than filled with mercury so that both the upper and lower meniscus are well within calibrated portions of the narrow ends. From the weight of this mercury—with proper correction for overlapping in the narrower calibrated parts—

the total capacity of the wider part of the tube is calculated. Two verifications of the correctness of the previous work are now undertaken. It will be noticed, on referring to Fig. II, that the upper scratch is not very far above the upper end of the wider portion of the manometer. The first step in the verification is to fill the space between the two scratches with mercury—the upper meniscus may extend somewhat above the upper scratch. The volume of this mercury should, of course, be equal to the sum of the previously found capacities of all individual parts which were filled by it. The final step in the verification is to apply the same test to the whole tube by filling it with mercury from the lower scratch to the upper limit of the calibration.

The statement given above is believed to be ample enough to afford an accurate general view of the method of calibrating. The details of manipulation and the precautions which it is necessary to take at various points are omitted. There is, however, one matter which requires further consideration, and that is the *meniscus*.

The method of obtaining the meniscus correction which is given above is believed to be entirely correct in principle, but in applying it, *we have never found the meniscus to have the spherical form* generally ascribed to it. Usually the correction for meniscus obtained by the method described is just about three-fourths what it would be if the form were truly spherical. Sometimes it is slightly less and sometimes slightly more, but the values of what we will call the *experimental* meniscus always hover around this proportion of a spherical one. We are by no means prepared to dispute the assumption generally made that the form of the meniscus in narrow tubes is spherical, for the deviation from it which we seem always to find may possibly be due to errors in reading the length of the short threads which are used in calibration. If these are read always *too short*, the obvious result would be a too small correction for the meniscus. The following observation is of some interest in this connection and may throw some light on the matter. A beginner in calibration usually derives from his measurements a smaller meniscus correction than one who has had more experience; but as he continues his work under proper supervision, his corrections increase in value up to the limit mentioned, and thereafter his results will accord well with those of other experienced observers. Whether we do or do not "read too short" in calibrating, we are inclined to think that it is safer for us to use the "experimental correction" than that which is derived from the supposed spherical form of the meniscus; since, whatever unconscious errors we make in reading the length of the calibrating threads, we would be likely to repeat in measuring pressure.

The importance of the part which meniscus correction has played in the recent measurements of osmotic pressure may be judged approximately from the following statements: The *mean* final number of calibration units of compressed nitrogen in the manometers, for all the measurements upon the 0.1 weight-normal solution (at 0°, 5°, 10°, 15°, 20°, and 25°), was 124.72 (a calibration unit being the volume of the gas in a length of tube equal to about 1 mm.). The *mean* of all the corrections for a double meniscus was 0.176 calibration unit. That is, the mean correction for meniscus amounted to 0.141 per cent. of the total volume of nitrogen. The mean osmotic pressure of this solution, between 0° and 25°, was 2.5 atmospheres. The value of the mean correction for meniscus, expressed in osmotic pressure, was, therefore, 0.0035 atmosphere.

In the case of the weight-normal solution, the mean volume of the nitrogen was 16.916 calibration units, while the mean of all the corrections for meniscus was 0.1807 calibration unit. That is, the mean correction for meniscus was 1.07 per cent. of the volume of the nitrogen. The mean osmotic pressure of the weight-normal solution between 0° and 25° was found to be 25.95 atmospheres. The average correction for meniscus, expressed in osmotic pressure, was, therefore, *0.278 atmosphere.* For solutions of intermediate concentration, the value of the meniscus correction, expressed in osmotic pressure, varied, of course, between these limits, *i. e.*, between 0.0035 and 0.278 atmosphere. Stated in another way, the correction for meniscus in our work varied from 0.141 to 1.07

per cent. of the magnitude measured, according to the concentration of the solutions.

The question now arises, To what extent may these corrections have been erroneous? If we admit a possible error of 25 per cent. in the correction for meniscus, which seems to be ample, the proper statement would be: "The uncertainties due to meniscus correction range, according to the concentration, between 0.0009 atmosphere for the most dilute and 0.07 atmosphere for the most concentrated solution; or, if expressed in percentage of the magnitude measured, between 0.035 and 0.27 per cent." We are inclined, however, to regard the allowance of 25 per cent. for possible meniscus error as too large, since we cannot understand how an error of this magnitude could accumulate. It has been found that the independent readings of a manometer by two or more experienced observers will rarely differ more than 0.01 mm. Allowing this difference to be error, it would, in the case of the normal solution, amount only to 5.5 per cent. of the mean meniscus correction. There is still, however, to be dealt with that unexplained difference between the "experimental" and the supposedly spherical meniscus. The usual difference here *is* about 25 per cent. of the latter; but, as stated before, if we unconsciously read "short" in calibrating, we should again read "short" in measuring a pressure, and there are no more readings involved in deriving an "experimental" meniscus correction than in measuring a pressure; that is, the errors in question are not really of a cumulative character, as one might suspect at first sight.

One advantage of this mode of deriving a meniscus correction which should be mentioned is the excellent means which it affords of detecting faulty calibration. It is known that the best work in calibration leads uniformly to an approximately fixed value for the meniscus; hence it is to be inferred when another value is obtained, that the calibration which gave it is erroneous.

The degree of the accuracy of the meniscus correction has, however, but little weight in settling the particular question which we have been trying to answer, namely, *the relation of* *pressure to temperature.* Here an error of 50 per cent. in the meniscus correction, if uniform, would scarcely influence the solution of the problem, since the magnitudes compared in any case—the pressures of a given single concentration of solution at different temperatures—differ but little. To illustrate this point, we will consider the osmotic pressures of the weight-normal solution between 0° and 25°. The pressures which were found are tabulated below, together with the ratios of osmotic to calculated gas pressure at the various temperatures. The pressures given are the means of all the individual results at each of the six different temperatures, and the corrections for meniscus are likewise the *means* of all the corrections which were actually applied in calculating those pressures:

I. Temperature.	II. Osmotic pressures. Atms.	III. Cor. for meniscus. Atm.	IV. Ratio osmot. to gas pressure.
0°	24.825	0.238	1.115
5°	25.283	0.306	1.115
10°	25.693	0.293	1.113
15°	26.189	0.242	1.115
20°	26.648	0.307	1.115
25°	27.053	0.257	1.113

Suppose now that the extreme possible error has been made, and that the meniscus corrections given in the third column are *erroneous to the extent of 100 per cent.*, the pressures in the second column being *too small* by that amount. The following table gives the results corrected in accordance with that supposition:

I. Temperature.	II. Osmot. pres. + meniscus cor.	III. Ratio osmot. to gas pressure.
0°	25.063	1.126
5°	25.589	1.129
10°	25.986	1.126
15°	26.431	1.125
20°	26.955	1.128
25°	27.310	1.124

The ratios of osmotic to gas pressure given in the last column still agree to the third decimal place, and practically the same temperature coefficient for osmotic pressure would be derived from the values in both tables.

In view of the situation as explained above, we think ourselves justified in the conviction that our main conclusion—as to the *equality of the temperature coefficients* of osmotic and gas pressures within certain limits—is not sensibly vitiated by any possible errors in meniscus correction.

It is seen that, in determining the temperature coefficient, the errors in meniscus correction, if they are uniform, may be very large without seriously affecting the result; but when it is attempted to ascertain the relation of osmotic pressure to *concentration*, the case is very different, for then the pressures of all the various concentrations of solution are to be compared at fixed temperatures, and the meniscus corrections have consequently widely differing values. This is illustrated by the following tabulation of data taken from the record of a single manometer (No. 9). The meniscus correction (double) in this instrument is 0.17 calibration unit, and the volume of the nitrogen under standard conditions of temperature and pressure is 454.14 calibration units. Column I in the table gives the weight-normal concentration of the solutions; II, the pressures in atmospheres; III, the volume of the compressed nitrogen reduced to standard temperature; IV, the corrections in fractions of an atmosphere for the double meniscus; V, the relative osmotic pressures, the pressure of the 0.1 normal solution serving as the unit. Column VI contains the relative corrections for meniscus, the correction for the 0.1 normal solution serving as the unit. The temperature is in all cases 25°.

I. Conc.	II. Os. pres. Atms.	III. Vol. N_2. cc.	IV. Menis. cor. Atm.	V. Rel. os. pres.	VI. Rel. menis. cor.
0.1	2.635	141.15	0.00317	1.0000	1.0000
0.2	5.139	80.69	0.01083	1.9503	3.4164
0.3	7.738	55.59	0.02366	2.9366	7.4637
0.4	10.295	42.41	0.04126	3.9070	13.0158
0.5	12.947	34.01	0.06972	4.9135	21.9937
0.6	15.620	28.37	0.09360	5.9275	29.5268
0.7	18.436	24.11	0.12999	6.9928	41.0063
0.8	21.258	20.97	0.17233	8.1055	54.3628
0.9	24.126	18.53	0.22133	9.1558	69.8202
1.0	27.076	16.54	0.27834	10.2755	87.8044

Particular attention is called to columns V and VI, where it will be seen that, while the osmotic pressure increased a little over tenfold, the value of the meniscus correction increased nearly *88-fold.* At first sight, this enormous disproportion between the increase in osmotic pressure and that of the meniscus correction is somewhat startling to one who does not have clearly in mind the fact that, though this, in the first instance, is simply a space of fixed volume, its importance depends not only on the pressure upon the gas which fills it, but upon the *volume* of all the gas in the manometer as well.

Expressed in heights of mercury column, the correction for meniscus in the cases cited in the table increases from a value of 2.4 mm. to one of 211.5, and it is just these highly variable corrections which must be applied to the magnitudes to be compared in determining the relation of osmotic pressure to concentration. It is for this reason principally that we do not regard such relations as are shown in column V as being established with as much certainty as we think we have established the temperature coefficient within the field over which we have worked. And it was principally in order to determine the relation of pressure to concentration with a higher degree of precision that the form of manometer shown in Fig. II was devised. One of its purposes, as will be readily seen, is to minimize the importance of the meniscus, especially for concentrated solutions, without much sacrifice of the advantages of tubes of small bore. In the instrument prepared for use with weight-normal solutions, the final length of the nitrogen column is about 10 times as great as it is in the manometer which has been used in the investigation of the temperature coefficient. The gain in the direction of greater precision is obvious.

When the calibration of the tube has been finished, it is fused to the bent bulb tube (Figs. I and II) and filled with nitrogen. The purification of the nitrogen and the filling of the manometer have already been described;[1] and since very little change has been made in the procedure in either case, the briefest possible outline of these operations will suffice.

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The gas is purified by passing air first through an alkalin solution of pyrogallol, and then, in the following order, ove heated copper oxide, heated copper, heated copper oxide fused calcium chloride, fused potassium hydroxide, and resublimed phosphorus pentoxide. The glass tubes containing the dry reagents are all connected with each other an with the receptacle for the nitrogen by fusing the ends together.

The apparatus used in filling the manometers is shown i Fig. IX. *A* is the reservoir for nitrogen. *B* is the manomete which is attached to the rest of the apparatus at *d* by fusin together the ends of the glass tubes. At the other end, th manometer is joined to the tube *C*, which serves as an ai reservoir to keep the pure mercury in the instrument separate from that which is used in the rubber tube and funnel arrangement which is seen to the right. The side tube *f* contains th mercury which is to follow the nitrogen and remain in the to of the tube when it is closed. The somewhat complex proces of washing and drying the manometer with purified air admitted through *h*, of replacing the air with nitrogen from th reservoir *A*, and of finally closing it with a short column o mercury in the top has been described in detail in the earlie paper on manometers. The only modification of the forme practice which has been found necessary is due to the introduction of traps in two of the bulbs. When a tube wit traps is first filled with mercury, minute quantities of air ar sometimes left between the mercury and the glass in the bottom of these bulbs; and, if the angle between the trap and th side of the bulb is a sharp one, it is often difficult to dislodg the entangled gas. Hence it is necessary, before attachin the manometer to the nitrogen reservoir, to fill the bulbs an to remove any air which is imprisoned in the manner described. If the mercury afterwards runs out of the bulbs no harm is done so long as the instrument is kept in the upright position, because the bulbs are then emptied only to th top of the traps. In the manometers recently prepared, th difficulty is overcome by giving a much flatter form to th bottoms of the bulbs with traps.

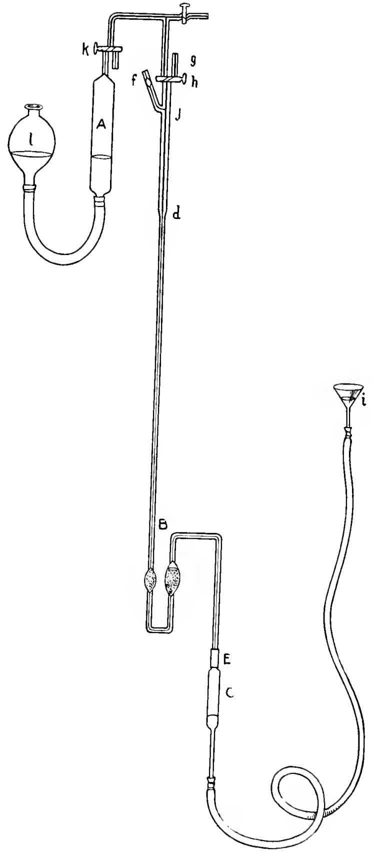

Fig. IX.

The volume of the nitrogen which has been introduced into the manometer is determined by means of the steel block. Formerly the instrument was placed in one of the three receptacles for tubes, and in another there was placed a piece which had been cut from the same tube, or, lacking this, another narrow tube in which the capillary depression had been determined at one or two points. If the piece of tubing which was to serve as a side tube was too short for the purpose, it was lengthened by fusing it to another similar tube. The third receptacle in the block was plugged with a glass rod or, preferably, occupied by another manometer—a so-called "standard" manometer.

The idea of using for the side tube a piece cut from the same tube as the manometer itself was, of course, that there would be no sensible correction for capillary depression. It was found, however, that the volume of the nitrogen—reduced to standard conditions—varied considerably with different positions of the meniscus, *i. e.*, with different pressures. In manometers of small capacity, these discrepancies have amounted, in extreme cases, to as much as one per cent. of the volume of the nitrogen. In the absence of any other known causes, it was necessary to ascribe such fluctuations in the apparent volume of the nitrogen to *variations in capillary depression* due to irregularities of bore. Moreover, it was apparent that in using a *narrow* side tube, we were in danger of multiplying, and possibly of more than doubling, the errors due to irregularities in the bore of the manometer itself. Hence, of late, when a nitrogen volume is to be determined, the narrow side tube is replaced by one having an internal diameter of about 30 mm., and much more attention is given to the investigation of the irregularities in the capillary depression of the manometers, that is, it is determined at many more points than formerly. The introduction of the wide side tube, in consequence of which only the errors of the manometer itself can now affect the results, has operated very favorably on the determination of nitrogen volumes, in that the volumes found under different pressures in any manometer are much more consistent than formerly.

We have used in our work until recently a so-called "standard" manometer. The third receptacle in the steel block was made for this instrument, and has most of the time been occupied by it. The "standard" differed from the other manometers, not in the pains which were taken with any one calibration, but in that the calibration was repeatedly verified. The use of the standard has not, however, given entirely satisfactory results. It has been impossible to make any other instrument conform to it absolutely. In other words, having found at some pressure the volume of the gas in a given instrument by means of the "standard," if we change the pressure, a slightly different value will be found, etc. The cause of the trouble is not difficult to discover. There is the same objection to the use of a "standard" manometer that there is to the use of a narrow "side tube," namely, that the results are vitiated by the errors of two instruments instead of one. It is for this reason that we now rarely use the "standard" manometer as a means of determining the volumes of gas in other instruments, or even for purposes of verification.

The difficulties which are encountered when a narrow side tube, or a standard manometer, is used reappear in full force when it is attempted to compare one manometer with another in the steel block, a practice very frequent in our earlier work, and still resorted to, but with less confidence than formerly. The osmotic pressures in duplicated determinations which are calculated from the original data of each instrument independently are rarely identical, as they should be. The discrepancies are not, however, large enough to weaken any general conclusions which may be based upon the measurements of osmotic pressure; but they suffice to explain, in large part at least, why it is that, with two perfect cells and two different manometers, we do not often appear to get quite the same pressures, though the concentration of the solution and the temperature are the same in both cases. It explains also why it is that duplicate measurements with one manometer generally agree better than those made with different instruments.

The necessity of making each manometer a law unto itself as regards accuracy, rather than subservient to some one standard for all, is unfortunate, for it greatly multiplies the pains and labor which must be bestowed on the individual instruments. The only alternative, however, appeared to be the employment of a "standard" with a bore wide enough to eliminate altogether the influence of capillary depression. The proper calibration and the use of such an instrument would obviously be attended with considerable difficulty, and we have not yet seen our way clear to undertake its preparation.

The following is a partial record of the capillary depressions which were found at different places in one manometer. The first column gives the distance above the lower scratch of the points at which the determinations were made, and the second, the depressions which were found at those points:

Distance above scratch.	Capillary depression.	Distance above scratch.	Capillary depression.
8.65	7.92	117.43	11.42
22.70	10.85	224.12	11.18
47.35	9.87	280.30	11.74
71.38	10.04	361.10	11.80
114.28	10.42	414.10	12.14

A difference of one mm. in capillary depression makes a difference of about one "calibration unit" in determining the volume of the nitrogen in a manometer. Suppose now the capillary depression of this tube had been determined only at the nine points beginning with the second one, 22.7 mm. above the scratch. The mean of these values is 11.05, which number would probably have been accepted as the *mean capillary depression* of the manometer. But suppose, when the volume of the nitrogen in the manometer is determined, the meniscus stands 8.65 mm. above the scratch, where the depression is 7.92 mm. The error, if the mean number 11.05 is used in correcting for capillary depression, is about 11.05 — 7.92 = 3.13 calibration units in the volume of the nitrogen. This example of what might happen if the condition of the tube at 8.65 mm. above the scratch had not been detected will serve to convince one, not only of the necessity of a most detailed investigation of the capillary depression in manometers of small bore, but also of the danger of using tubes of small bore or even "standard" manometers as "side tubes" when a nitrogen volume is to be determined. The whole volume of gas in the tube in question was 400 calibration units, hence the possible error in the case cited is 0.78 per cent., but to this there would have been added any errors of a *narrow* side tube, whether the same was originally a part of the same tube as the manometer itself, or a so-called "standard" manometer.

Capillary depression appears twice as an important factor in a measurement of osmotic pressure: (1) in determining the volume of the nitrogen under standard conditions of temperature and pressure, and (2), in correcting its volume under an unknown pressure which is the quotient of the two volumes.

The single illustration given above will suffice to give an idea of the possibilities in the way of error which pertain to tubes of small bore in consequence of their large and irregular capillary depression; and it will explain, in a measure also, why we felt obliged to confess at the beginning of this paper that, after ten months of labor bestowed on them, we were still dissatisfied with the manometers which were used in the attempt to determine the temperature coefficient of osmotic pressure. We were trying all of this time to use "standard" manometers and other tubes of small bore as "side tubes." The course to which we have finally been driven by the discrepancies which appeared is the one which we ought to have followed from the first, and would have followed if we had realized in the beginning the importance of the *variability* of capillary depression even in the most perfect tubes of small bore. The present procedure, so far as capillary depression is concerned, is as follows:

1. The tubes are calibrated with the utmost care with respect to capillary depression, that is, the capillary depression is determined at a great number of points in a tube, and a depression curve is made out which is quite as detailed as the curve for volume.

2. In determining the volume of nitrogen in manometers, the use of narrow side tubes and of other manometers has been abandoned, and only very wide tubes (30 mm. internal diameter) are employed for the purpose.

3. As in the case of meniscus, the relative effect of variable capillary depression is diminished by increasing the volume of the nitrogen. That is, the form of manometer shown in Fig. II has been adopted for the purpose of minimizing the importance of capillary depression, as well as that of meniscus.

4. Because the unknown errors of two instruments always add themselves in any direct comparison, the *verification* of one manometer by means of another (a "standard") has been given up, except as a means of detecting large errors, whatever may be their nature.

The question has arisen in our minds whether the slow contraction in glass, which is observed in thermometer bulbs, and which results in an upward displacement of the zero points, may not also affect our manometers, causing the volume of the nitrogen apparently to increase with time. We have been trying for two years to secure evidence on this point, but have been unable thus far to come to any definite conclusion. The trouble has been that the small differences which were apparently observed *might* be due to undiscovered irregularities in capillary depression. An effect of this kind is to be watched for, especially in the most recent form of manometer, where a wide tube is fused in between two narrower ones. These tubes are, however, annealed with care, and they are also allowed to lie for several months before a calibration is undertaken.

In conclusion, we will state that the whole time of one of the authors of this paper (C.) is given up to the study of the manometers which have been or are to be used in our measurements of osmotic pressure, and that we feel assured that no possibility of any very large error in this department of the work has escaped detection.

Johns Hopkins University,
December 24, 1910.

VISCOSITY AND FLUIDITY OF MATTER IN THE THREE STATES OF AGGREGATION AND THE MOLECULAR WEIGHT OF SOLIDS.

BY EUGENE C. BINGHAM.

[TENTH COMMUNICATION BEARING ON THIS SUBJECT.]

Introduction.

It is highly advantageous to consider the properties of matter under as varied conditions as possible. Many properties, however, are not as satisfactory in this respect as viscosity, which can be applied to all three states of matter. But, although it is now clear that gases and liquids and amorphous solids pass into each other without any sharp line of demarcation, when we come to consider the viscosity of matter in the three states of aggregation there are some very striking contrasts.

In liquids, the viscosity decreases with elevation of the temperature without a single exception; in gases, the opposite is the case without exception. In liquids, the viscosity seems to vary greatly with the density; in gases, the viscosity is independent of the density within wide limits. In liquids, the viscosity increases with the molecular weight; in gases, the molecular weight is of uncertain influence.

So with solids, the damping of the vibrations of a wire varies largely from substance to substance and with the temperature. This damping is of course far greater than can be accounted for by the friction of the air or by the loss of energy to the support. Hence this phenomenon, first studied by Weber, has been regarded by many, notably Lord Kelvin, as due to internal friction analogous to the internal friction or viscosity of liquids. Now it has never been made clear whether or not this *elastic after-effect*, as it is called, is in truth a measure of viscosity; and, as we shall see, there have even been some who have preferred to keep the two entirely distinct. In spite of this uncertainty, it seems clear that this loss of energy in vibrating is a true *frictional effect*. If, however, we regard it as a *measure* of the viscosity of solids, which appears to be the more usual practice, we find again a marked contrast with the viscosity of liquids with which it is supposed to be analogous.

In liquids, the viscosity decreases rapidly as the temperature is raised; in solids, the viscosity, as measured by the rate of damping of the vibrations of a wire, increases rapidly with the temperature. In liquids, the viscosity of a given liquid is constant for a given temperature and pressure. The fact that chrome alum solutions and some others suffer a change of viscosity on boiling, as well as a change of color and doubtless other properties, might be cited as exceptions to this, but the exceptions are not real because the different hydrates may properly be regarded as distinct compounds with their own properties. In solids, however, such exceptional behavior is the rule. It has been found that the viscosity as measured by the damping is greater when the wire is first loaded or if the wire is hardened, as in drawing. Rapid heating and cooling of the wire decreases the viscosity. Briefly, the viscosity of metals depends largely upon their history as well as upon their actual condition, which is thus quite in contrast with the behavior of liquids and gases, except for the readily explained exceptions noted above.

In our study of viscosity it now seems necessary, before proceeding further, to frame a hypothesis which will enable us to form some conception of the nature of the above phenomena and which will coördinate the apparently disconnected facts and suggest further study.

The Theory of Viscosity in Gases.

For gases, the kinetic molecular hypothesis is sufficient for the explanation of the principal facts, as is well known. If a gas is flowing over a plane surface, the gas which is actually in contact with the surface may, generally speaking, be considered to be at rest, since the smoothest surface must be considered quite rough in this connection. It has been proved that the velocity of the gas increases directly proportionally to the distance from the surface. Suppose A and B

in Fig. I to be two layers of gas so thin that the translational velocity within each layer may be assumed to be constant. Let A be moving toward the right with a velocity very slightly greater than B. As the particles of the gas are moving in every direction, those of A will sometimes pass over into B, carrying with them not only their momentum due to their irregular motion, which is the same in both layers, but also the momentum due to the drift of A over B. Conversely, when particles of B pass over to A there will also be an expenditure of momentum required to impart to them the unidirectional motion of the drift. Thus, unless force is continually applied to A, it will come to have the same motion as B, *i. e.*, the unidirectional motion will all be changed into irregular molecular motion or heat.

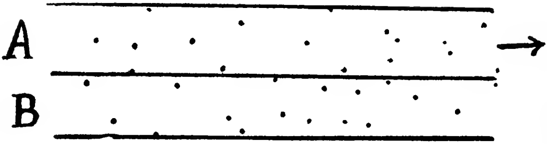

Fig. I.

As the temperature is raised, the irregular motion of the molecules becomes increased and the rate of loss of momentum is increased, *i. e.*, the viscosity is increased.

The fact that the viscosity of gases is independent of the density within wide limits was predicted by Maxwell as a deduction from the kinetic molecular hypothesis, which had been recently proposed. Its later verification by experiment constituted one of the chief arguments for the acceptance of the kinetic theory and is perhaps the most notable triumph yet achieved in the study of viscosity. The reason why the density of a gas does not affect the viscosity may be readily perceived. For as the density of the gas is decreased the same number of molecules cross the boundary between A and B, the only difference being that they come from a greater depth. This will not be true, however, when the molecules cross the confining space without encounter, and this breaking down of the law at very low pressures has been abundantly proved by experiment.[1] So also as the density is increased the mean paths become shorter and shorter but the number of molecules crossing the boundary between *A* and *B* remains the same, but this probably ceases to hold as the volume of the molecules becomes appreciable in respect to the spaces between them, or as the attraction between the molecules becomes appreciable, or, in other words, as Boyle's law ceases to hold.

The Theory of the Viscosity of Liquids.

For liquids, no consistent theory has been worked out, although oftentimes their viscosity has been referred to the attraction between the molecules. It does not appear, however, that such a theory can be worked out or that the attraction between the molecules in itself will suffice to explain the facts in regard to the viscosity of liquids. If in Fig. II we assume that *A* and *B* represent layers of liquid within which the velocity may be regarded as constant, while between *A* and *B* there is a very small velocity, then the conditions may be sufficiently well represented for our present purpose, which is rather to lay the basis for future work than to attempt a rigid mathematical presentation. The single molecules are to be considered as bodies of some appreciable size as compared with the spaces between them, although the question as to shape is left open. We must also assume that there is some attraction between the molecules, as proved by cohesion. Since the molecules are so much closer together than in the gas, the paths of the individual molecules must be

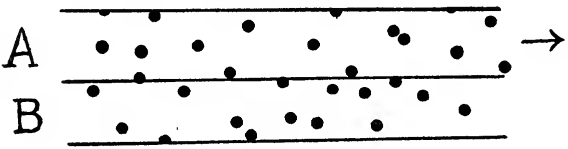

Fig. II.

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[1] Kundt and Warburg: Pogg. Ann., **155**, 337 and 525 (1875); **156**, 177 (1875).

exceedingly short, hence molecules with considerable translational velocity are unable to penetrate to layers with much lower translational velocity, so that the cause of viscosity in gases is not very potent in liquids.

Since the mean speed at any given temperature must remain the same, the number of molecules crossing the boundary between *A* and *B* will hardly be increased by any attraction between the molecules. Moreover, the forces of attraction are the same in every direction, so that no work is done within the liquid, and it is not apparent how the forces between the molecules can affect the viscosity.

Let us now digress for the moment to speak of external friction in order to obtain an analogy between external and internal friction that may be of service. If one body is resting upon another, forces of the nature of adhesion are exerted between the two, although for the most part the bodies will be separated by a layer of the atmosphere in which the bodies are immersed, but they will also come into contact at a few points. If force sufficient to cause the one body to move over the other is applied, the force required to keep the motion uniform is proportional to the force pressing the two bodies together, but it is independent of their size or their velocity, within certain limits, so long as the surfaces are the same; the smoother the surface, the less the friction. This much has been made clear as the result of a large amount of work. The friction is due to a variety of causes: (1) At the start adhesion has to be overcome to *separate* the particles which were in immediate contact, but after motion is established the force required to maintain the motion becomes less, and it is perhaps doubtful if the adhesion between the surfaces plays an important part. (2) Indirectly, however, cohesion plays an important part, for as the parts projecting from the opposite surfaces collide, particles are torn away, overcoming the forces of cohesion between them. (3) When a hammer strikes an anvil, a good part of its kinetic energy is transformed into waves of condensation and rarefaction which finally may be dissipated in heat. So as a solid moves over another, the projections of the one striking the projections of the other give rise to vibrations which may finally result in sound, light, electricity, or heat. Most of the friction apparently results from this last cause.

I believe that we may regard liquid viscosity or internal friction as the analogue of external friction, for if we think of the particles of A moving ever so slightly faster than those of B, then the particles of B near the boundary will be overtaken by those of A, and the latter will impart momentum to the former. The particle which has been thus overtaken, as in external friction, need not be carried along. It may first suffer a displacement, causing a condition of strain to be set up in its neighborhood. This strain later results in an increased molecular motion in B. It is this weakness of liquids in suffering displacement under stress that differentiates them from solids, but the line of demarcation is imperceptible. I shall speak later in this paper of the strain thus set up. According to this conception, the viscosity of liquids is not primarily dependent upon their cohesion, but upon the *volume* of the individual molecules, for the chances of collision between molecules of A and B will depend upon the ratio of the volumes of the molecules to the spaces between them. I use the term molecule, particle, or aggregate here without distinction. We might even include the term crystal with these when speaking of solids.

Connection between the Viscosity of Liquids and Molecular Volume.

It is evident that as the volume of the spaces between the molecules is still further decreased, the number of collisions will be increased. This is in harmony with the fact that in all liquids, without hardly an exception, the viscosity increases as the temperature is lowered, for the volume of liquids is thus generally decreased. Of course, if a change of molecular weight occurs, we may expect irregularity, hence we need not be unduly disturbed by such an abnormality as is shown in the density of water at 4°. In general, the relation holds good that as liquids expand the viscosity decreases. This is true, moreover, whether the expansion results from an elevation of temperature or a lowering of the pressure. Here again, however, water is abnormal at low temperatures, but the apparent exception can here be explained in the same way. It has been shown with certainty that viscosity increases with molecular weight, each atom having its own particular influence; and it appears that some groupings are of influence, the substance which has the more compact grouping having the least viscosity. Associated compounds have increased viscosity proportional to their association.[1] Colloidal substances, which have very large molecular weights, exert enormous influence upon the viscosity of their solutions. So also in mixtures, when liquids mix without marked volume change, the fluidities are a linear function of their composition[2], as we might expect. As far as I have been able to ascertain, whenever there is a marked contraction on mixing, as is true in very many aqueous solutions, there is invariably a marked decrease in the fluidity below what might be expected from the linear rule. In one instance I have observed that an increase of fluidity, in a similar manner, is connected with an increase in volume. It is regrettable that there are so few data with which to test this point. Yet various observers in other connections have noted a relation between viscosity and volume.[3]

In a recent paper[4] I pointed out that at some temperature near the critical temperature, the temperature coefficient of fluidity must be zero, *i. e.*, the fluidity must reach a maximum. The data of Warburg and Babo[5] enable us to say that for carbon dioxide such a maximum exists, within the limits of observational error, at the critical temperature and that for liquids, even in this limiting condition at the critical temperature, so long as the volume is constant the viscosity is independent of the temperature. While for gases the viscosity is independent of the volume within wide limits, for liquids the

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[1] Bingham and Miss Harrison: Z. physik. Chem., **66**, 1 (1909). Bingham: THIS JOURNAL, **43**, 287 (1910).

[2] Bingham: THIS JOURNAL, **35**, 195 (1906).

[3] Warburg and Sacho: Wied. Ann., **22**, 518 (1884). Bingham: THIS JOURNAL, **43**, 287 (1910).

[4] THIS JOURNAL, **43**, 295 (1910).

[5] Wied. Ann., **2**, 406 (1877).

viscosity is apparently dependent primarily upon the volume. In gases the viscosity is dependent primarily upon the momentum of the molecules; in liquids, I have tried to show that it is dependent primarily upon the volume of the molecules.

The Theory of the Viscosity of Amorphous Solids.

For amorphous solids one would expect the same relations to hold as for liquids, since amorphous solids are nothing more than undercooled liquids. The difference should be one of degree only. As the temperature is lowered, the molecules continually get closer and closer, thereby circumscribing more and more each other's motion. The molecules, in suffering displacement, cause a state of strain to be established, as was pointed out above. As the cohesion of the substance increases, the stress which will be necessary to cause the displacement necessary for viscous flow also increases.

It should be noted here that if the displacement of a particle of B is sufficiently violent to cause it to be permanently displaced among its neighbors in that layer, the motion is no longer linear, and eddy currents are formed; and this motion does not obey the same laws as when the motion is linear, as has been abundantly verified. If, on the other hand, the stress accumulates faster than can be accommodated by the gradual breaking down of the strains here and there in the different layers of the substance, as has been explained, then the cohesive power of the substance will be exceeded and rupture will occur. In a rather viscous substance these accumulated strains may be observed, if the stress is removed quickly enough, by the springing back of the substance in the opposite direction to the stress. Moreover, this recoil will obey the laws of viscous flow in that its velocity will be directly proportional to the distance from the surface over which the fluid is moving and the velocity will be directly proportional to the strain. This recoil is the analogue of the "Weber effect" or "elastic after-effect" or "accommodation" in metals. Fortunately, this effect has also been observed for undercooled liquids as well. Barus[1] has measured the viscosity of marine

[1] Am. J. Sci., [3] **45**, 87 (1893).

glue by forcing it through a narrow tube after the method of Poiseuille. The glue was cut off at the opening of the tube, a series of cylinders being thus obtained. By weighing these, the rate of transpiration was determined. But the remarkable thing is that these cylinders did not keep their original cylindrical form, but a motion of the central axis of the cylinder, which continued for many hours, took place in the direction opposite to the stress, as shown in Fig. III. Trouton and Andrews[1] determined the viscosity of solid substances such as pitch and glass by continually twisting a rod or tube made of the material. They found that after the stress was removed there was a movement in the reverse direction for a long time. They then took the stress off as such a rate that there would be no movement at all. In this way the stress remaining at any given moment was a measure of the remaining after-strain. Plotting the time elapsed against the stresses, they obtained a rectangular hyperbola. Their experiment shows that the velocity of flow is proportional to the pressure, and the experiments of Barus indicate that the velocity is proportional to the distance from the surface over which the movement takes place.

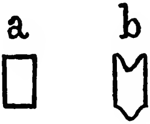

Fig. III.

As we may infer from the above and as I have pointed out elsewhere,[2] the fluidity of an undercooled liquid ought to approach the zero value asymptotically. So now we get a conception of the entire fluidity curve of a substance in relation to the temperature, as shown diagrammatically in Fig. IV. Starting with what must be practically zero fluidity at absolute zero of temperature the fluidity increases very slowly with the temperature from *A* to *B*, more rapidly from *B* to *C*,

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[1] Phil. Mag., [6] **7**, 347 (1904).

[2] Z. physik. Chem., **66**, 238 (1909).

as a linear function of the temperature over a range *C* to *D*, then less and less rapidly, finally becoming constant at the critical temperature *E*, and from that point decreasing over a range *F* to *G*, which has been explored. Beyond this we have

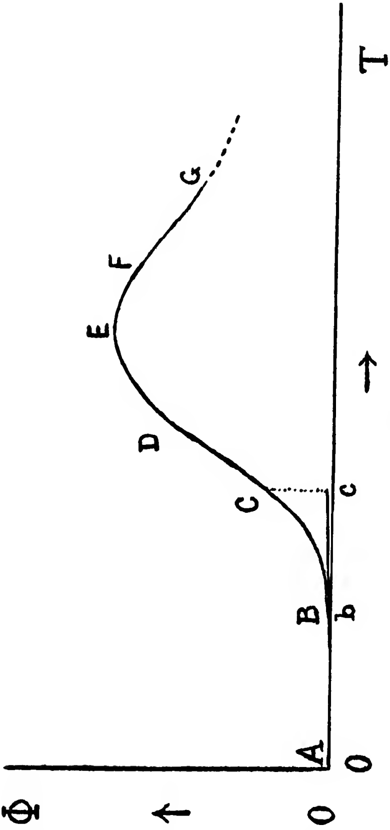

Fig. IV.

no information, but it seems unthinkable, with our present knowledge, that a gas can become very rigid at even an exceedingly high temperature, hence we may assume that the curve does not cut the temperature axis at any point *H*. Substances are commonly regarded as solids over the range *AB*, as liquids over the range *BE*, and as gases from *E* on.

The Theory of the Viscosity of Solids.

We now will consider the solid state, meaning, by the term, the crystalline solid. We immediately see that in addition to the above curve, there must be for the crystalline solid another curve with very much lower fluidity over part of its course. This curve is entirely independent of the curve of the undercooled liquid, and corresponds to a substance with a very much greater molecular weight, this increase taking place at the time of solidification. This is shown in the curve *A b c*, Fig. IV.

Now turning to the case of wires subjected to torsional vibrations, we observe that the amplitudes of the vibrations form a geometrical series, hence the logarithmic decrement of the vibrations is the quantity which is usually sought. It has been found by Guye and Mintz,[1] as a result of their own experiments and of those of their predecessors, that if a wire is reheated with its maximum load, it will give a logarithmic decrement which is constant for a considerable amplitude at a given temperature, and the value is the same regardless of whether the immediately preceding values were at a lower or at a higher temperature. As was remarked at the beginning of this paper, there has been a tendency to consider this logarithmic decrement as a measure of the viscosity of solids analogously with the viscosity of liquids. This will be made clear from the following definition of the viscosity of solids taken from Thomson and Tait's *Treatise of Natural Philosophy*,[2] "A distinct frictional resistance against every change of shape is demonstrated by many experiments, and is found to depend on the speed with which the change of shape is made. A very

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[1] Arch. sci. phys. nat., [4] **26,** 136 and 263 (1908).

[2] Vol. I, pt. 2, p. 303.

remarkable and obvious proof of frictional resistance to change of shape in ordinary solids is afforded by the gradual, more or less rapid, subsidence of vibrations in elastic solids; marvelously rapid in India rubber and even in homogeneous jelly; less rapid in glass and metal springs, but still demonstrably much more rapid than can be accounted for by the resistance of the air. The molecular friction in elastic solids may be properly called *viscosity of solids*, because, as being an internal resistance to change of shape depending upon the rapidity of change, it must be classed with fluid molecular friction, which by general consent is called the *viscosity of fluids*." But even they recognized that the matter was not clear.

Now it happens that steel and quartz show the smallest amount of damping, while a soft metal like lead shows a far greater amount. That lead can be considered to have a greater viscosity than hard steel, the term "viscosity" being used in its ordinary meaning, seems quite unbelievable. The difficulty is increased if we recall that the logarithmic decrement increases very rapidly with the temperature for most substances, and Guye and Freedericksz have shown[1] that at absolute zero of temperature the logarithmic decrement must become very nearly zero. This would correspond to infinite fluidity, which is certainly opposed to our usual conception of fluidity. Therefore it seems clear that although the damping of a vibrating wire is undoubtedly due to internal friction or viscosity, it cannot be used as a direct measure of that quantity.

If a filament of a perfectly elastic substance, to which quartz is the best approximation, were twisted away from its position of rest, it would come back to its original position even after the stress had been applied for a very long time; or if allowed to vibrate, it would swing back and forth for a very long time before coming to rest, the only losses of energy being to the support and the surrounding viscous medium. If an imperfectly elastic filament, like glass, be used, when it is twisted from its position of rest it will receive a "set," but if the stress is applied for a short time only, the set will be for the most

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[1] Compt. rend., **149**, 1066 (1909).

part of a temporary character, and the glass will gradually creep back to nearly its old position of rest. This is the "elastic after-effect" of Weber. If glass then is allowed to vibrate transversely, the zero point O, in Fig. V, at the end of the first swing to the left is changed to O', consequently, after the point, O' is passed, in returning the wire moves the remainder of the distance to O at the expense of its own momentum. Similarly at the end of the swing to the right the zero point has been changed to O'', and so on.

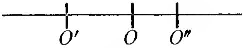

Fig. V.

It now becomes possible to form a conception of the phenomena taking place in a vibrating wire, and in elastic solids generally, on the basis of what we have learned from the viscosity of fluids. In twisting a wire, we can see from symmetry that the particles must move in circles, which are cross-sections of the wire, provided that the wire is round and homogeneous. Thus Fig. VI will represent a portion of a cross section, the layer B being the nearer the center. If the molecules of A move over B until the stress just balances the external force without the stress being relieved by even a partial breaking down of the material, then there will be no loss of energy by internal friction and when the external force is removed the material will return to its original position. In other words, if the molecules of A push against those of B but fail to pass them, as they do pass in the case of viscous flow, then the material is perfectly elastic. But it seems likely that all substances with which we are acquainted will

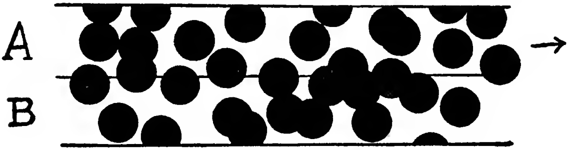

Fig. VI.

flow like liquids if sufficient pressure is applied for a long enough interval of time. The pressure which is necessary to make the flow perceptible is the "elastic limit," but the flow is so very slight that a wire loaded to the elastic limit may still bear a somewhat increased load without at once breaking, so that the "yield point" lies somewhat beyond the elastic limit. When this point is reached the wire is no longer able to sustain even its former load and rupture takes place as explained earlier. According to this conception the greater the damping the greater is the *fluidity* of the substance! This view is in harmony with the fact that the logarithmic decrement increases with the temperature, for the fluidity may be expected to increase as the molecular distances are increased. Further tests of the above hypothesis as applied to solids will be given further on.

Having already reached the above conclusion in regard to the error of regarding the logarithmic decrement as a measure of viscosity or internal friction in solids, I was delighted to find that Kuppfer, as early as in 1861, had held the view that the damping of a wire is a measure of its fluidity and stated it in such a convincing manner that Pearson at a much later date, 1893, recognized the difficulty of regarding the after-strain as a measure of viscosity, and advised against it in the following words: "It seems difficult to me to identify frictional resistance and elastic after-strain."[1] He goes on to say that "the creeping back to the original shape which goes on, it may be for minutes, hours, or even days, after the removal of the load, can hardly be due to frictional action," but, as we have seen, the work of Barus and of Trouton and Andrews throws a flood of light on this point. This difficulty in regard to elastic after-strain also troubled Kuppfer, for he says: "Die Nachwirkung bringt hier dieselbe Wirkung hervor, wie die Friction beim Widerstande der Luft, und besteht wohl auch in Nichts anderem, als in einem mit Friction verbundenen Glitschen der Theile über einander: nur ist nicht zu übersehen, dass die Friction der Theilchen unter

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[1] Todhunter and Pearson: "The History of the Elasticity and Strength of Materials," Vol. II, pt. 2, Sec. 1718, p. 419.

einander nicht zu erklären im Stande ist, warum der Stab oder der Draht, nach Aufhebung der ablenkenden Kraft, wieder zu seinem ursprünglichen Gleichgewichtszustande zurückkehrt; diese Erscheinung setzt offenbar eine gewisse Kraft voraus, welche jeden festen Körper, selbst wenn er durch Änderung seiner Form in andere Gleichgewichtsbedingungen versetzt worden ist, dennoch immer wieder in längerer oder kürzerer Zeit zu seiner ursprünglichen Form (oder zu seinen ursprünglichen Gleichgewichtsbedingungen) zurückfährt, wenn die Abweichung von der ursprünglichen Gleichgewichtslage nicht gar zu gross gewesen ist."[1] This statement by Kuppfer causes Pearson to remark that "This passage seems to me to mark off the real distinction between after-strain and any frictional action between the parts of the body, and I think destroys the force of the comparison of a solid body's elastic after-strain with fluid action. It is a strong reason for not allowing elastic after-strain to be masked under the term viscosity." I believe that all of the difficulties are removed by means of a conception like the one that I have outlined. How clear Kuppfer's conceptions were for the time in which he wrote may be inferred from the following: "Il paraît que les molécules des corps solides possèdent la propriété non seulement de s'écarter les unes des autres en produisant une résistance proportionelle aux écarts, mais aussi de glisser les unes sur les autres, sans produire aucun effort. Cette propiété est possédée à un haut degré par les fluides; je le nommerais volontiers la fluidité des corps solides; le coefficient ψ pourrait être appelé coefficient de fluidité; la malléabilité des métaux paraît en dépendre et peut-être aussi leur dureté; des expériences ultérieures nous apprendront jusqu'où va cette analogie."[2]

We use the term fluidity in respect to solids as did Kuppfer and note with him that there are other terms in use which are evidently closely related, as malleability, pliability, and softness, while the reciprocals of these find expression in the

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[1] Mém. Acad. St. Pétersburg sci. math. phys., [6] **6**, 397–494 (1857).

[2] Recherches expérimentales sur elasticité des métaux faites à l'observatoire physique central de Russie, p. 50 (1860).

terms viscosity, internal friction, rigidity, and hardness. Elasticity of shape seems to depend not only on a high viscosity, but also directly on the cohesion between the molecules. Barus seems to have regarded the two as merging into each other, believing that the more highly viscous a substance is the greater is its elasticity of shape. There appear to be, however, four categories into which substances fall, depending upon the possession to greater or less degree of the above two properties. (1) There are substances possessing high cohesion and high viscosity, as steel and quartz. (2) There are others possessing high cohesion but relatively low viscosity, as India rubber. (3) Substances with low cohesion and low viscosity are represented by most liquids and gases; while (4) there are substances of low cohesion and high viscosity, as is the case with many inorganic salts, like sodium chloride which has not been made to flow even under the highest attainable pressure.

Rubber is highly elastic yet the damping of its vibrations is marvellously rapid, showing a high degree of fluidity. The easy elongation of rubber is also an evidence of its fluidity. There is the utmost range in both of these properties so that all of the above examples are not equally good and it may be said that most substances fall between the extreme cases enumerated.

Finally it will be worth while to test the above hypothesis to see if it will explain the peculiar behavior of solids.

(1) Increase in temperature will cause the molecules to be separated, generally speaking, so that the fluidity will be increased, which has been found true for a considerable number of substances, as marine glue,[1] ice, glass,[2] and, as we have seen, the same is probably the case with most metals. Quartz is exceptional in this respect but its expansion coefficient is also exceptional, which may provide an explanation.

(2) Pressure has the effect of decreasing the fluidity, as we would expect. Barus has shown that for marine glue the effect of one degree rise in temperature requires the effect of

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[1] Barus: Phil. Mag., [5] **29**, 337 (1890).

[2] Trouton and Andrews: *Loc. cit.* Weinberg: Ann. Physik. [4] **18**, 81 (1905).

many atmospheres of pressure to counteract it. This is in accordance with the relative effects of temperature and pressure on volume.

(3) Repeated heating and cooling, according to Horton,[1] causes a decrease in the logarithmic decrement which may be interpreted as due to the increase in the elasticity of the metal, on account of the removal of the strains originally present.

(4) When a wire is first loaded strains are developed, hence vibrations take place by means of viscous flow to a larger extent than after the wire has hung for a long time when the strains have become more equally distributed. So the logarithmic decrement decreases with time.[2]

(5) For large amplitudes of swing the logarithmic decrement is greater than for small amplitudes,[3] because the nearer the limit of elasticity is approached the greater will be the amount of motion of the viscous kind.

(6) But if the vibrations are continued rapidly for a long time residual strains will accumulate to such an extent that elastic motion will be largely prevented, giving a state of "elastic fatigue" discovered by Lord Kelvin. Thus a steel tuning-fork vibrated continuously for many hours will reach a state where it will hardly vibrate at all, as has come under my own observation.

(7) Heating will dissipate the above "fatigue" because thereby the strains are removed. Resting will accomplish the same result, in the course of time, by means of the more leisurely viscous flow at the lower temperature.

(8) Trouton and Andrews[4] have shown that if a rod of such solids as glass, pitch, etc., be twisted with sufficient force, the parts of the rod may be made to move continuously over each other with a velocity which is greatest at first but gradually decreases to a constant value. This is explained by the after-strain requiring time to reach its maximum, just as we have seen that it dies away slowly in these substances.

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[1] Phil. Trans. (London), **204,** A, 1 (1904).

[2] Guye and Mintz: Arch. sci. phys. nat., [4] **26,** 136 and 263 (1908).

[3] Guye and Mintz: *Loc. cit.*

[4] Phil. Mag., [6] **7,** 347 (1904).

Other tests of a similar character will readily suggest themselves, such as the cause of the increase in strength of wires on drawing. It even becomes possible to form a conception of the perplexing behavior of plastic substances, like clay, which do not yield at all until a certain pressure is reached, when they yield rapidly. The resistance at first is probably due to the adhesion between the particles. This adhesion will be the more considerable, because the particles are very small and their surfaces correspondingly great. When, however, the particles become separated, the resistance is largely dependent upon the viscosity of the medium filling the spaces between the particles, as, for example, water, in the case of plastic clay. The fluidity of mixtures of substances which are insoluble in each other presents a very interesting field for study. Moreover it has important technical bearings, as in the manufacture of paints, lubricants etc. One phase of this subject is now being studied experimentally by Dr. George F. White and myself.

In conclusion, I venture to express the belief that the viscosities of solids may be measured in such a way as to obtain results which are comparable with those obtained for liquids and gases. For undercooled liquids the methods of the falling sphere and of forcing the liquid through a capillary tube have been tried with success.[1] The viscosity of the more highly viscous bodies may probably be measured by the methods tried by Trouton and Andrews, of continuously twisting a rod or tube, of determining the sagging of a beam, or finally of measuring the vibration of a wire.

If these methods can be made to give comparable results, as has been indicated by the work of Trouton for all except the last method, then it seems quite possible to solve the problem of obtaining the molecular weights of solids, which has baffled us thus far, since the method of getting the molecular weights of liquids by means of their viscosities[2] has been found to give good results.

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[1] The latter method has been applied to metals by Werigin, Lewkojeff, and Tammann: Ann. Physik, [4] **10**, 647 (1903).

[2] Bingham: Z. physik. Chem., **66**, 238 (1909).

THE DISSOCIATION OF ELECTROLYTES IN NONAQUEOUS SOLVENTS AS DETERMINED BY THE CONDUCTIVITY AND BOILING-POINT METHODS.

By Henry R. Kreider and Harry C. Jones.

Four methods have been devised for measuring the dissociation of salts in solution: The conductivity and freezing-point methods, the solubility method of Nernst and Noyes, and the boiling-point method. Of these the conductivity and freezing-point methods are the best known, and are the most accurate. The solubility method of Nernst and Noyes is not widely applicable. Within recent years the boiling-point method has been so much improved by Jones and others that it gives fairly accurate results.

There are certain objections to all of these methods. The conductivity and the freezing-point methods give good results in aqueous solutions, but in nonaqueous solutions which are less dissociated, their use has been attended with difficulty. In many of these solvents it has not been possible, previous to the present time, to determine μ_∞ accurately, and, consequently, the dissociation could not be calculated from the results obtained by the conductivity method. Many of the nonaqueous solvents freeze at a temperature so far below the ordinary that the application of the freezing-point method is often impossible.

By means of the latest type of cell devised in this laboratory, and which will be described later, we have been able to measure μ_∞ for a number of salts in methyl and ethyl alcohols, and thus to calculate the dissociation of these salts in these solvents from the data obtained by the conductivity method. The dissociation of these same salts in the same solvents was determined by the boiling-point method with the object of finding if any relation exists between the results obtained by the two methods.

HISTORICAL REVIEW.

A large amount of work has been done with nonaqueous solvents, especially with the lower alcohols of the aliphatic series. These were soon found to have the property of dissociating salts to a considerable extent. Fitzpatrick[1] studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride and calcium chloride in both methyl and ethyl alcohols, and found values which were considerable, though less than those in water. Hartwig[2] measured the conductivity of a number of organic acids in both methyl and ethyl alcohols. Paschow[3] worked with potassium iodide, cadmium iodide, calcium iodide, potassium acetate and sodium acetate in methyl alcohol. Vicentini[4] measured the conductivities of a number of salts of these alcohols. Cattaneo,[5] working with salts in ethyl alcohol, found that a number of those with which he worked have a negative temperature coefficient in this solvent. Vollmer[6] studied several salts over a large range of dilutions. Holland[7] investigated the effects of non-electrolytes on the conductivity of various salts in methyl alcohol. Carrara's[8] work is very important. He carried out an extensive investigation on a large number of salts in methyl alcohol. Walden[9] did a large amount of work with pure organic solvents. The work of Dutoit and Aston[10] and of Frederich[11] is important. They formulated the hypothesis that the dissociating power of a solvent is a direct function of its degree of association in the pure state. Other workers in this field are Kablukoff,[12] Vollmer,[13] and Kahlenberg and Lincoln.[14]

Mixed Solvents.

Wakeman[15] carried out an investigation on organic acids in

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[1] Phil. Mag., **24,** 378 (1893).
[2] Wied. Ann., **33,** 58 (1888); **43,** 838 (1891).
[3] Charcow, 1892.
[4] Beibl., Wied. Ann., **9,** 131 (1885).
[5] *Ibid.*, **18,** 219, 365 (1894).
[6] Wied. Ann., **52,** 328 (1894).
[7] *Ibid.*, **50,** 263 (1893).
[8] Gazz. Chim. Ital., [1] **26,** 119 (1896).
[9] Z. physik. Chem., **5,** 35 (1890).
[10] Compt. rend., **125** 240 (1897).
[11] Bull. Soc. Chim., [3] **19,** 321 (1897).
[12] Z. physik. Chem., **4,** 432 (1889).
[13] Wied. Ann., **52,** 328 (1894).
[14] J. Phys. Chem., **3,** 26 (1899).
[15] Z. physik. Chem., **11,** 49 (1893).

mixtures of water and ethyl alcohol and found that the conductivity of these substances in these solutions decreased with increasing amounts of alcohol. Zelinski and Krapiwin[1] point out that the salts with which they worked, the iodides and bromides of sodium and ammonium in mixtures of 50 per cent. methyl alcohol and water, give a conductivity considerably less than the conductivity of these salts in either pure alcohol or water. Cohen[2] gives similar results with ethyl alcohol and water, and finds that potassium iodide in 80 per cent. alcohol shows a larger conductivity below $V = 512$ than in pure alcohol, but at a greater dilution the conductivity is less in the mixed solvents than it is in either of the pure solvents. Wakeman,[3] working with mixtures of ethyl alcohol and water, found that the equation,

$$\frac{\Delta}{p(100 - p)} = \text{constant}$$

held for many substances in mixtures of the above-named solvents (Δ is the difference between the conductivity of the electrolyte in water and in the mixture, and p the percentage of alcohol by volume).

From his own and from Wakeman's observations Cohen points out the following relation:

$$\frac{\mu_v \, H_2O}{\mu_v \, H_2O.\text{Alc.}} = \text{constant.}$$

This relation holds independently of temperature and concentration. He remarks that either the dissociation of the salt with which he worked is the same or that in these mixtures conductivity is not a direct measure of dissociation. Roth later found that the relation given by Wakeman holds, while that given by Cohen does not.

Jones[4] and his coworkers have done a fairly large amount of work on conductivity and viscosity in mixed solvents. Since the following is essentially a continuation of that work a very brief review of the latter is necessary.

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[1] Z. physik. Chem., **21**, 35 (1896).

[2] *Ibid.*, **25**, 31 (1898).

[3] *Ibid.*, **11**, 49 (1893).

[4] Publication No. **80**, Carnegie Institute.

Jones and Lindsay[1] found that the phenomenon discovered by Zelinski and Krapiwin is not confined to a few salts in mixtures of methyl alcohol and water only, but that it holds over a large range of salts and also in ethyl alcohol-water mixtures. It holds less generally at 25° than at 0°, and in ethyl alcohol-water mixtures less than in methyl alcohol-water mixtures. The conductivities were always less than the mean calculated from the conductivities in the pure solvents.

As a partial explanation they advance the following tentative suggestion: According to the theory of Dutoit and Aston only the polymerized molecules of the solvent dissociate the molecules of the solute. It is well known that water and the alcohols used are highly associated substances. On coming into contact with each other, they break down the association of each other until equilibrium is reached; and, consequently, they have less dissociating power. In methyl alcohol-water mixtures where association of the constituents is greatest the dissociation is greatest. Other facts are in accordance with this suggestion. Since at the lower temperatures the association is greatest in the constituents, we would expect the greatest abnormality here. And such is the case.

These conclusions were subsequently further confirmed by the cryoscopic work of Jones and Murray.[2] They worked with water and formic and acetic acids, and determined the molecular weights of each in the other by the freezing-point method. They found that the molecular weights of these substances are always less than the molecular weights of the pure substances as determined by the method of Ramsay and Shields. They thus conclude that the action of an associated solvent upon another associated solvent is analogous to the action of an associated solvent upon an electrolyte.

Jones and Carroll[3] extended the work of Jones and Lindsay. They worked with both binary and ternary electrolytes. As solvents they used methyl and ethyl alcohols and mixtures of these two. Acetic acid was also used. In mixed solvents

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[1] THIS JOURNAL, **28,** 329 (1902). Z. physik. Chem., **56,** 129 (1906).

[2] THIS JOURNAL, **30,** 193 (1903).

[3] *Ibid.*, **32,** 521 (1904).

a minimum was found with the following salts: cadmium iodide, sodium iodide, and hydrochloric acid in mixtures of ethyl alcohol and water. That of cadmium iodide exists for dilutions up to 50 only, at 0°; beyond that there is no minimum. At 25° there is no minimum.

Somewhat surprising results were found with hydrochloric acid in methyl alcohol and water mixtures; μ_∞ occurs at very low dilutions in mixtures containing up to 90 per cent. alcohol (between V 100 and V 200), while in 100 per cent. methyl alcohol it is not found even as high as V 2104. In the dilutions above these limiting values there is a decrease in conductivity.

The relation pointed out by Wakeman,

$$\frac{\Delta}{p(100 - p)} = \text{constant},$$

does not hold; neither does that of Cohen.

They explain the cause of the minimum as follows: There are two factors which determine conductivity, the amount of dissociation and ionic mobility. Decrease or increase of either of these produces a corresponding result in the conductivity.

They point out that there is a close connection between the fluidity and conductivity of a solution. These vary directly. When the solutions are brought together there is an increase in viscosity, or decrease in fluidity, which is its reciprocal. Consequently, the ions are much retarded in their movements and the conductivity diminished. As the temperature rises there is a shifting of the minima towards that mixture containing the greatest percentage of alcohol. In this shifting, however, the fluidity minima, they state, lag behind the conductivity minima.

They propose the following hypothesis: "The conductivities of comparable equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohol, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficients of viscosity of the solvent in question, and directly proportional to the association factor of the solvent in question." These conclusions may be formulated as follows:

$$\frac{\mu_v}{x} = \text{constant, or } \frac{\mu_v \eta}{a} = \text{constant.}$$

The work of Jones and Bassett[1] with silver nitrate in both methyl alcohol-water and ethyl alcohol-water mixtures deals with the same phenomena as were previously discussed. There are well marked minima in the curves at both 0° and 25° in methyl alcohol-water mixtures, but no such minima occur in ethyl alcohol-water mixtures. In all cases, however, the curves fall much below the straight line of averages.

Jones and Bingham[2] measured the conductivities of lithium nitrate, potassium iodide, and calcium nitrate in water, methyl and ethyl alcohols and acetone, and binary mixtures of these solvents. They also made a large number of viscosity measurements of pure solvents, of mixed solvents, and of electrolytes in solution. In acetone and water mixtures the same minima which previous workers had observed were also observed. While the conductivity minima are intimately related to the minima of fluidity, the conductivity curves of different salts show marked differences. In acetone and alcohol mixtures the curves conform to the law of averages, that is, the conductivity curves are nearly straight lines. From this fact they conclude that the mixtures do not form more complex molecular aggregations.

A peculiar fact, and one not previously known, was here discovered. Lithium and calcium nitrates in mixtures of acetone with methyl or ethyl alcohol present a very pronounced maximum of conduction. This must be due to one of two causes: There is either an increase in dissociation and, consequently, an increase in the number of ions present, or there must be a diminution in the size of the ionic spheres, causing them to move more rapidly. We eliminate the first cause since fluidities of mixtures of acetone and the alcohols obey the rule of averages. This would indicate that there is no increase in the molecular aggregation in these mixtures, and

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[1] This Journal, **32**, 409 (1904).

[2] *Ibid.*, **34**, 481 (1905).

according to Dutoit and Aston's hypothesis such a mixture would not dissociate to a greater extent than the constituent solvents. Since we can eliminate increased dissociation as the cause of the maximum, it must be due to the change in the dimensions of the ionic spheres. The previous work of Dutoit and Friederich and of Jones and Carroll is incomplete since it does not take into consideration the size of the ionic spheres.

The tendency to show maxima in conductivity increases from potassium iodide through calcium nitrate to lithium nitrate, which seem to show these effects most strongly. This may be connected with the ionic velocities, since potassium is a small ion and a comparatively rapidly moving one, and lithium forms, by combination with the solvent, a large ion and one that moves more slowly.

Jones and Rouiller[1] worked with silver nitrate in the solvents used by Jones and Bingham. In a general way they found results similar to those previously obtained. There is a striking similarity in the curves at 0° and 25° in mixtures of ethyl alcohol and acetone. There is a pronounced maximum at both 0° and 25° in the 25 per cent. acetone mixture in the more concentrated solutions, and shifting with increase in dilution through the 50 per cent. mixture to the 75 per cent. mixture. For pure acetone these curves decline rapidly. For mixtures of methyl and ethyl alcohols, the curves are nearly straight lines following the fluidity curves.

Jones and McMaster[2] worked with lithium bromide and cobalt chloride in the same solvents that had been employed by Bingham. The fluidities of water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents were measured. The conductivities of these mixtures with water show a well-marked minimum. This minimum shows an intimate relation to that of fluidity. Lithium bromide in mixtures of methyl and ethyl alcohols gives no minimum in conductivity. The curves are nearly straight lines, except at the higher concentrations where there is a slight sagging

[1] THIS JOURNAL, **36**, 42 (1906).

[2] *Ibid.*, **36**, 325 (1906).

at both temperatures. The same salt shows a maximum in conductivity in acetone-methyl alcohol mixtures with 75 per cent. acetone. The maxima increase with rise in temperature. In acetone-ethyl alcohol mixtures the same characteristics are manifested.

Cobalt chloride in methyl alcohol-water mixtures shows minima at both temperatures. At the higher temperature the minimum is most marked with 75 per cent. alcohol. In mixtures of ethyl alcohol and water, this salt shows a point of inflection at both temperatures and at all dilutions. These results are similar to those obtained by Jones and Bingham with calcium nitrate in acetone-water mixtures. In ethyl alcohol-methyl alcohol mixtures there is no distinct minimum but a sagging of the curve.

The minimum of fluidity corresponds to that of conductivity. There is in both methyl alcohol-water and ethyl alcohol-water mixtures a tendency of the minimum to shift towards the mixture containing the greatest percentage of alcohol whenever there is a rise in temperature. The authors reach the conclusion suggested by former workers that a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum in conductivity; and that the change in the size of the ionic spheres or the atmosphere which surrounds the ions should also be taken into account.

Several points in connection with the temperature coefficients are important. In nearly every case the temperature coefficients are smaller in the more concentrated solutions. Jones had already explained the phenomena in the following manner: In practically all solutions there is combination between solvent and solute. As dilution increases the solvates become more complex. Change in temperature affects most greatly the complex solvates, therefore we should expect the largest temperature coefficients at high dilutions.

At certain concentrations in methyl alcohol and acetone a negative temperature coefficient manifests itself. Conductivity varies directly as dissociation and fluidity. Since rise in temperature diminishes dissociation, and increases fluidity, it would seem that there would be a point where these two influences would equalize each other, and the temperature coefficient become zero. This concentration is reached at *V* 200 in a 75 per cent. acetone and methyl alcohol mixture. Beyond this dilution there is a negative temperature coefficient.

Jones and Veazey[1] measured the conductivities and viscosities of solutions of copper chloride and potassium sulphocyanate in water, methyl alcohol, ethyl alcohol and acetone, and binary mixtures of these solvents. The minimum which was previously observed with different electrolytes is here also observed in some cases. This minimum is more pronounced at the higher dilutions. Where no minimum occurs there is a decided fall below the average value for the pure solvents. There is an interesting difference in the values for molecular conductivity in the pure solvent with increasing dilutions. In pure water, copper chloride, a ternary electrolyte, shows a much greater conductivity than potassium sulphocyanate, a binary electrolyte. In pure methyl alcohol the opposite condition exists. The conductivity of potassium sulphocyanate is the greater. This fact appears in previous work. Ethyl alcohol shows the same phenomenon.

The temperature coefficients of conductivity increase with increase in dilution. There is one exception—cobalt chloride in methyl alcohol. A marked negative temperature coefficient of viscosity is shown by potassium sulphocyanate in aqueous solutions.

In a recent communication Jones and Veazey[2] report the results of a study of solutions of tetraethylammonium iodide in mixtures of water, the alcohols and nitrobenzene. In mixtures of the alcohols and water there is a well-defined minimum in conductivity. In mixtures of the alcohols with each other there is no minimum, although the curves fall below the averages. In methyl alcohol and nitrobenzene the same phenomena occur, but in ethyl alcohol and nitrobenzene there is

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[1] This Journal, **37**, 405 (1907). Z. physik. Chem., **61**, 41 (1908).

[2] This Journal, **41**, 433 (1909).

a maximum. The conductivity curves correspond very well with the fluidity curves.

Jones and Mahin[1] took up the study of cadmium iodide and lithium nitrate in binary mixtures of water, methyl and ethyl alcohols and acetone, and lithium nitrate in ternary mixtures of these solvents. Viscosity measurements of these solutions were also made. These measurements were carried to as high dilutions as possible—in some cases as high as 200,000 liters. At these high dilutions it was impossible to prevent considerable error due to the large correction for the specific conductivities of the solvents, and the large cell constants. With lithium nitrate the product of viscosity and molecular conductivity is nearly a constant for mixtures of acetone with methyl alcohol and ethyl alcohol. This value is independent of the temperature. The value is nearly 0.70, which is Walden's value for tetraethylammonium iodide. With acetone-water mixtures the product varies between 1.00, the value for water, and 0.63, the value for acetone.

Interesting results were obtained by determining the molecular weights of lithium nitrate in acetone by the boiling-point method. The object was to test the assumption that the low conductivity of this salt in ordinary solutions is due to the association of the salt. In the most dilute solution—0.09 normal—which could be determined accurately, the boiling-point method showed a molecular weight of 83.1, while the normal molecular weight is 69.07. We can, therefore, conclude that there is association, and this would account for the low conductivity in solutions at great dilutions.

Jones had already shown that cadmium iodide in acetone is associated. This salt was next investigated and found to behave like lithium nitrate in its molecular conductivity. There is an irregularity in the product of conductivity and viscosity in acetone and methyl alcohol mixtures, while in the pure solvents these products are nearly the same. In acetone-ethyl alcohol mixtures there is a fair degree of constancy in these products. Jones has shown that there is considerable polymerization of cadmium iodide in acetone.

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[1] Z. physik. Chem., **62**, 41 (1908).

Conductivity and viscosity in ternary mixtures of the above solvents were next taken up, and a considerable amount of work was done. The object was to determine whether any essentially new pricinples could be discovered by increasing the number of components in the solvent mixture. The results are about what we would expect from a knowledge of the behavior of solutions in binary solvent mixtures.

Turner,[1] working in Jones's laboratory, made various conductivity measurements of potassium iodide, lithium chloride and lithium bromide in pure ethyl alcohol, at high dilutions. Many precautions were pointed out which were very helpful in the present work. The purification of solvents, precautions necessary to prevent contact with foreign substances, and other sources of error were investigated and discussed in detail. After repeated experiments it was found that small traces (0.2 to 0.3 per cent.) of water do not appreciably affect the conductivity.

The conductivity of potassium iodide in ethyl alcohol was measured up to a dilution of 450,000 liters. A maximum of molecular conductivity of 48.5 was reached at about 20,000 liters. From this the ionization was calculated. Measurements of conductivity were made at as high as 78°. The temperature coefficients increase with increasing temperatures and with increasing dilution. Ionization decreases considerably with rise in temperature. A 0.1 normal solution is dissociated 49 per cent. at 0°, 46 per cent. at 25° and about 35 per cent. at the boiling point of ethyl alcohol.

Determinations of ionization were also made by the boiling-point method, but these are in all cases considerably lower than those obtained by the conductivity method.

The work of Jones and Schmidt[2] introduces a new solvent, *glycerol*. They measured the conductivity and viscosity of lithium bromide, cobalt chloride, and potassium iodide in glycerol, methyl and ethyl alcohols, and binary mixtures of these and water. Glycerol was employed as a solvent because of its high viscosity. Its dielectric constant is about

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[1] This Journal, **40**, 558 (1908).

[2] This Journal, **42**, 37 (1909).

one-fifth that of water and it ought to have a fairly high dissociating power. It has remarkable solvent properties. But little work had previously been done with glycerol as a solvent. For measuring viscosity a viscometer with especially large bore had to be constructed.

Measurements of conductivity were made at 25°, 35° and 45°. Lithium bromide in mixtures of glycerol with water, methyl alcohol, and ethyl alcohol shows no minimum, but there is a wide departure from the law of averages, and a marked sagging in the curves. We would hardly expect a minimum since there is probably no mixture of glycerol with these other solvents which is more viscous than glycerol itself.

With cobalt chloride the conductivities in pure glycerol increase regularly. The conductivity values are considerably higher than the corresponding values for lithium bromide. Since cobalt chloride is a ternary electrolyte and lithium bromide a binary one, these results are just what we should expect. In pure ethyl alcohol, however, the case is different. The values for the conductivity of cobalt chloride are abnormally low. Lithium bromide, for instance, in a 0.1 N solution has a molecular conductivity of 15.8 at 25°. We should expect that cobalt chloride, since it is a ternary electrolyte, would have a conductivity probably 50 per cent. greater, but the value for the molecular conductivity of cobalt chloride in ethyl alcohol at the above concentration is only 4.71. Many of the halides of the heavy metals tend to form complexes when dissolved in organic solvents. It was supposed that the low conductivity of cobalt chloride in ethyl alcohol, at least in the more concentrated solutions, was due to polymerization of the molecules. Molecular weight determinations of cobalt chloride in ethyl alcohol were made by the boiling-point method. The mean of three determinations is 140 at about one-twelfth normal concentration, while the molecular weight for the compound $CoCl_2$ is 129.9. This would seem to indicate that there is association and, consequently, a lower conductivity than would be expected.

Potassium iodide in glycerol behaves like the other salts. There is a slight increase in conductivity with dilution. In each case the conductivities for mixed solvents are less than the average for pure solvents.

A new feature is the magnitude of the temperature coefficients of conductivity. Some are almost as high as nine per cent. Cobalt chloride in ethyl alcohol manifests a negative temperature coefficient. A negative viscosity manifests itself in the case of potassium iodide in water, and in 25 per cent. and 50 per cent. glycerol and water at both 25° and 35°.

An elaborate investigation has been carried out in this laboratory during the past year by Guy on glycerol as a solvent. The results of this work will soon be published.

EXPERIMENTAL.

This investigation was undertaken for the purpose of obtaining facts by means of which the following questions might be answered:

1. At what dilutions do the maxima in conductivity occur for various salts in methyl and ethyl alcohols?
2. Is there any relation between these maxima in conductivity for different salts in different solvents?
3. What is the magnitude of the dissociation of these salts in these solvents as calculated by means of the maxima in conductivity?
4. What relation does this dissociation bear to that found by means of the boiling-point method?

Apparatus.

The Kohlrausch method was used. The wire was calibrated and was found to be of uniform thickness throughout.

The cells were of the latest type used in this laboratory. They were devised for measuring the conductivity of very dilute solutions where there is great resistance. They consist of two concentric platinum cylinders so placed one within the other that the electrodes are only about 1 mm. apart. They are held together by means of small drops of fusion glass placed between them. These electrodes have a surface of about 48.75 square cm. One of these cells had a constant as low as 2.82. The vertical position of the electrodes permitted the ready escape of all air bubbles, neither were they difficult to wash and dry if the proper precautions were observed. These cells gave excellent results, and a sharp minimum was obtained upon the bridge without difficulty. The constants were determined by means of 0.01 N and 0.001 N solutions of potassium chloride. These constants were frequently redetermined but were found to change but little throughout the work.

All the appparatus was carefully calibrated. The necessary precautions concerning temperature were observed. The temperature in the 25° bath was regulated with a sensitive thermometer calibrated against a German Reichanstalt thermometer. The 0° bath was from time to time tested to see that there was no change in temperature. At no time were measurements made when the temperature varied more than 0°.04 from that required. Careful tests were made to find the time required for the temperature of the solutions within the cells, both at 0° and 25°, to reach an equilibrium. This equilibrium was indicated by a constant conductivity. In all cases nearly an hour was necessary. Three readings were always taken and the mean was employed.

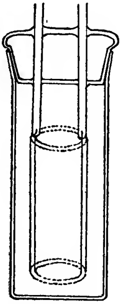

Fig. I.—Type of cell employed in this work.

For 0° measurements a battery jar filled with ice and water was placed within a bucket and surrounded with ice and water. The cells were placed in the battery jar and covered with glass. Ample time was allowed for the temperature to reach an equilibrium. Frequently the first reading was repeated after an interval of fifteen minutes or more, insuring equilibrium.

Extreme precautions were necessary in washing the apparatus. No fumes were permitted in the room. Immediately before using, the cells and flasks were thoroughly washed with distilled water, then rinsed several times with conductivity water and finally washed repeatedly with alcohol. This alcohol was always kept pure and used only a few times before it was dried and redistilled. Ether was not employed in drying since there is danger of fats being contained in it. The apparatus was then carefully dried. Before a solution was made up in a flask the latter was rinsed with a portion of the solvent, and the cell was rinsed with a portion of the solution. In many cases of very dilute solutions the flask in which the solution was to be made up was first cleaned, dried and rinsed with alcohol, the conductivity of this alcohol determined, and this same alcohol was employed to dilute the solution and its conductivity was used for the correction for the specific conductivity of the solvent. As a rule, there was little change in this conductivity when the above precautions were observed, and yet, because of the large volume, this change was at times quite appreciable.

Salts.

The salts used were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, copper chloride, calcium nitrate and cobalt chloride.

In all cases the necessary precautions were observed in purifying the salts, Kahlbaum's best products being employed. All were recrystallized a number of times, finally from conductivity water and some from absolute alcohol. All were dried at a temperature of 125°–150°. Those which are very deliquescent were heated for a long time, some for several days, in an air bath. Those chlorides which readily form oxychlorides when heated in the air were recrystallized several times, then dried in a vacuum desiccator over sulphuric acid for several days, and finally heated for a long time in a current of dry hydrochloric acid gas. They were then placed in a desiccator over sulphuric acid and potassium hydroxide for several days. All other salts but the latter class were dried to constant weight before making up each solution.

Solvents.

The solvents used were methyl and ethyl alcohols and mixtures of these with water. Considerable difficulty was experienced in purifying methyl alcohol so as to obtain it with as low a specific conductivity as possible. This low conductivity was important since there was danger of introducing considerable error due to the large correction for the specific conductivity of the solvent at these high dilutions. It was evident from the results that some foreign substance was contained in the methyl alcohol which it was difficult to remove. It was supposed that this unusually high conductivity was due probably to pyridine bases, and that these might be removed by treatment with sulphuric acid. The cold alcohol was treated with a small quantity of dilute sulphuric acid. It was then distilled, the first runnings being always discarded, and the receiver removed while a considerable quantity was still in the flask. The alcohol was then boiled with lime for a day and distilled. In some cases it was repeatedly treated with lime and repeatedly distilled. One quantity thus treated gave a conductivity as low as 7.1×10^{-7}. On standing, however, the conductivity changed somewhat, so that not all work was done with alcohol having quite such low conductivity.

The ethyl alcohol was distilled from lime several times, then repeatedly distilled until it had a conductivity of about 2.6×10^{-7}. The water was purified by the method of Jones and Mackay.

Solutions.

All solutions were made by direct weighing. In those cases where the solutions were to be very dilute and but a small quantity of the salt was needed, a 0.1 N solution was made as a mother solution. This was then diluted to a second mother solution. From this the final dilutions were made directly. Only in a few cases was a final dilution made from any other but the first or the second mother solution.

All solutions were made up at 20°. Enough time was always allowed for the temperature to come to equilibrium. The solutions when once placed in the cells were not removed from them until after measurements were made for both temperatures. They were never left in the cells longer than necessary because of possible decomposition:

Table I.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	69.05	96.18	0.01572
2048	70.62	99.22	0.01620
4096	71.48	101.14	0.01660
8192	72.13	102.4	0.01679
16384	74.5	104.8	0.01627
32768	76.6	107.2	0.01598

Table II.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	23.4	36.4	0.02222
2048	28.6	44.9	0.02280
4096	29.4	47.2	0.02422
8192	32.7	47.5	0.01810
16584	32.5	47.4	0.01834
33168	32.0	47.2	0.01900

Table III.—Conductivity of Ammonium Bromide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	66.1	93.1	0.01634
2048	69.9	94.1	0.01377
4096	70.6	96.7	0.01482
8129	71.8	96.8	0.01393
16584	69.2	94.9	0.01485

Table IV.—Conductivity of Ammonium Bromide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	32.1	37.0	0.02047
4096	25.2	39.6	0.02285
16384	27.5	39.1	0.01687
65536	29.8	39.5	0.01302

Table V.—Conductivity of Potassium Sulphocyanate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	69.1	98.3	0.01690
3200	71.1	101.0	0.01682
12800	73.0	103.7	0.01682
25600	83.5	106.3	0.01092

Table VI.—Conductivity of Potassium Sulphocyanate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	28.2	43.8	0.02218
3200	28.6	45.7	0.02391
6400	29.2	46.67	0.02393
12800	29.23	45.4	0.02213
25600	28.57	43.64	0.02110

Table VII.—Conductivity of Lithium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	58.83	83.24	0.01659
3200	59.89	85.98	0.01743
6400	61.46	89.29	0.01811
12800	59.69	91.35	0.02121
25600	60.36	93.61	0.02203

Table VIII.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	23.82	36.67	0.02157
3200	24.13	38.44	0.02372
6400	25.63	40.87	0.02378
12800	25.87	40.02	0.02187
25600	...	43.30	0.00000

Table IX.—Conductivity of Sodium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	60.32	87.67	0.01814
1024	64.15	90.91	0.01669
2048	63.65	91.93	0.01777
4096	63.34	91.06	0.02382
8192	65.90	93.40	0.01669
16384	63.1	91.8	0.01819

Table X.—Conductivity of Sodium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	24.41	38.06	0.02237
1024	25.12	39.66	0.02315
2048	25.89	40.92	0.02322
4096	26.89	41.84	0.02224
8192	26.06	42.86	0.02579
16384	26.79	42.02	0.02274
32768	28.83	43.22	0.01996

Table XI.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	83.53	106.04	0.01078
3200	93.50	120.58	0.01156
6400	105.46	138.46	0.01252
12800	112.52	151.73	0.01394
25600	119.44	164.6	0.01509
51200	124.58	175.0	0.01620

Table XII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	17.19	24.48	0.01696
3200	19.11	29.52	0.02179
6400	21.45	34.16	0.02370
12800	24.22	39.23	0.02537
25600	27.61	45.67	0.02616
51200	31.92	51.62	0.02469

Table XIII.—Conductivity of Cobalt Chloride in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	101.94	138.58	0.01438
3200	110.98	152.34	0.01878
6400	115.76	162.38	0.01612
12800	116.22	165.74	0.01704
25600	115.34	166.08	0.01760
51200	112.58	157.96	0.01614

Table XIV.—Conductivity of Cobalt Chloride in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	19.99	25.61	0.01125
3200	22.75	30.13	0.01298
6400	25.68	34.15	0.01319
12800	29.25	39.01	0.01335
25600	31.36	43.62	0.01564
51200	31.62	46.31	0.01858
102400	28.42	(52.26)	0.00000

Table XV.—Conductivity of Copper Chloride in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	64.13	78.58	0.09013
3200	75.43	89.31	0.07361
6400	85.22	101.28	0.07538
12800	91.3	112.3	0.09201
25600	90.5	116.4	0.01145
51200	79.1	112.1	0.01669

Table XVI.—Conductivity of Copper Chloride in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	16.08	20.96	0.01214
3200	18.94	25.74	0.01436
6400	21.06	30.70	0.01831
12800	22.52	34.16	0.02067
25600	22.94	37.79	0.02589

Table XVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	45.03	90.44	0.04023
2048	44.26	91.60	0.04278
4096	45.60	92.80	0.04140
8192	45.56	92.40	0.04112
16384	48.60	96.0	0.04000
32768	51.99	100.7	0.04517

Table XVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	35.77	72.24	0.04078
2048	36.07	73.37	0.04137
4096	37.49	74.64	0.03968
8192	38.04	76.20	0.04013
16384	40.18	79.9	0.03945
36768	46.86	93.1	0.03948

Table XIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	41.63	71.37	0.04952
2048	41.20	72.00	0.05064
4096	41.82	73.19	0.05247
8192	44.98	75.41	0.05475
16384	46.83	75.3	0.05339
32768	49.95	71.8	0.01910

Table XX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	32.38	74.80	0.05241
2048	32.75	76.23	0.05311
4096	32.73	76.60	0.05361
8192	33.88	77.20	0.05115
16584	35.30	80.3	0.05138
33168	39.88	86.8	0.04702

Table XXI.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.04	52.12	0.06401
2048	20.92	52.83	0.06073
4096	21.28	53.20	0.06000
8192	21.34	54.09	0.06120
16384	20.94	55.23	0.06550
32768	23.10	59.16	0.06244

Table XXII.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.58	44.14	0.04579
2048	21.39	45.04	0.04423
4096	21.50	45.91	0.04541
8192	21.34	45.96	0.04615
16384	21.85	47.85	0.04760
32768	23.68	51.04	0.04491
65536	25.11	53.30	0.04491

Table XXIII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	66.85	144.1	0.04620
3200	68.20	148.5	0.04831
6400	69.39	151.8	0.04749
12800	70.50	152.3	0.04641
25600	72.08	159.0	0.04823
51200	80.30	181.6	0.05046

Table XXIV.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	53.94	113.5	0.04417
3200	55.84	115.7	0.04287
6400	56.59	119.4	0.04440
12800	57.86	122.3	0.04456
25600	58.70	124.1	0.04457
51200	65.2	138.6	0.04503

Table XXV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	56.23	101.5	0.03220
3200	63.32	115.4	0.03290
6400	64.22	118.1	0.03356
12800	66.48	120.7	0.03262
25600	66.2	122.3	0.03390
51200	69.0	124.9	0.03241

Table XXVI.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	47.92	119.7	0.05992
3200	49.08	123.6	0.06072
6400	50.80	127.4	0.06032
12800	50.73	129.7	0.06227
25600	51.83	135.0	0.06419
51200	57.74	154.4	0.06697
162400	60.20	170.5	0.07327

Table XXVII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.16	81.56	0.06469
3200	32.27	84.67	0.06495
6400	32.70	86.56	0.06588
12800	33.70	88.28	0.06479
25600	33.25	87.42	0.06517
51200	34.18	90.8	0.07743
102400	34.40	89.7	0.07609

Table XXVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.0	67.1	0.04658
3200	32.4	70.5	0.04704
6400	33.1	73.4	0.04870
12800	33.7	74.6	0.04855
25600	34.4	74.8	0.04698
51200	34.0	72.4	0.04518

Table XXIX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	45.0*	35.8	41.6*	69.1
2048	88.5	44.3	36.1	41.2	70.6*
4096	88.9	45.6	37.5	41.8	71.5
8192	89.2*	46.6	38.0*	45.0	72.1
16384	89.2	46.6	40.2	46.8	74.5
32768	89.2	52.0	46.9	49.9	76.6

Table XXX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	90.4	72.2	71.4	96.2
2048	136.2	91.6	73.4	72.0	99.2
4096	136.7	92.8*	74.7	73.2	101.1
8192	136.9*	92.4	76.2	75.4*	102.4
16584	136.9	95.3	79.9	75.3	104.8
33168	136.9	100.7	93.1	71.8	107.2

Table XXXI.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	32.4	20.0	20.6	23.4
2048	88.5	32.8*	20.9	21.4	28.6
4096	88.9	32.7	21.3*	21.5*	29.4
8192	89.2*	33.9	21.3	21.3	32.7*
16584	89.2	35.3	20.9	21.8	32.5
33168	89.2	39.9	23.1	23.7	32.0
65536	....	....	....	25.1	....

Table XXXII.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	74.1	52.1	44.1	36.4
2048	136.2	76.2	52.8	45.0	44.9
4096	136.7*	76.6	53.2	45.9	47.2
8192	136.9	77.2	54.1	46.0*	47.5
16584	136.9	80.3	55.2	47.9	47.4*
33168	136.9	86.8	59.2	51.0	47.2

Table XXXIII.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	66.9	53.9	56.2	101.9
3200	68.2	55.8	63.3	111.0
6400	69.4	56.6	64.2	115.8
12800	75.5*	57.9	66.5*	116.2*
25600	72.1	58.7	66.2	115.3
51200	80.3	65.2	69.0	112.6

Table XXXIV.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	144.1	113.5	101.5	138.58
3200	148.5	115.7	115.4	152.34
6400	151.8	119.4	118.1	162.38
12800	152.3	122.3	120.7	165.74
25600	159.0	124.1	122.3	166.1
51200	181.6	136.6	124.9	158.0

Table XXXV.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	47.92	31.16	31.0	19.99
3200	49.08	32.27	32.4	22.75
6400	50.80*	32.70	33.1	25.68
12800	50.73	33.70*	33.7	29.25
25600	51.83	33.25	34.4*	31.36
51200	57.74	34.18	34.0	31.62*
162400	60.20	34.40	....	28.42

Table XXXVI.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	119.7	81.56	67.1	25.61
3200	123.6	84.67	70.5	30.13
6400	127.4	86.56	73.4	34.15
12800	129.7	88.28	74.6	39.01
25600	135.0	87.42	74.8	43.62
51200	154.4	90.8	72.4	46.31

Table XXXVII.—Dissociation of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	100.0	94.2	100.0	97.8
2048	99.2	...	95.0	...	100.0
4096	100.0	...	98.7	...	...
8192	...	...	100.0	...	...

Table XXXVIII.—Dissociation of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	98.7	93.9	95.8	71.5
2048	99.2	100.0	98.1	99.5	87.4
4096	100.0	100.0	100.0	100.0	90.0
8192	...	...	...	...	100.0

Table XXXIX.—Dissociation of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	88.6	...	84.5	87.6
3200	...	90.3	...	95.1	95.5
6400	...	91.9	...	96.5	99.6
12800	...	100.0	...	100.0	100.0

Table XL.—Dissociation of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	94.2	92.5	93.0	63.2
3200	...	96.6	95.7	94.1	72.0
6400	...	100.0	97.0	96.2	81.2
12800	...	...	100.0	97.9	92.5
25600	...	...	...	100.0	92.2
51200	...	...	...	...	100.0

Table XLI.—Maxima in Molecular Conductivity for Certain Salts in Pure Alcohols.

	0°.	25°.
KI in methyl alcohol	(77.5)	(112.6)
KI in ethyl alcohol	32.7	47.5
NH_4Br in methyl alcohol	71.8	96.8
NH_4Br in ethyl alcohol	(30.3)	39.6
KCNS in methyl alcohol	(69.2)	(110.4)
KCNS in ethyl alcohol	29.2	46.7
$LiNO_3$ in methyl alcohol	61.5	(96.7)
$LiNO_3$ in ethyl alcohol	25.9	40.8
NaI in methyl alcohol	64.1	91.9
NaI in ethyl alcohol	27.0	42.8
$CuCl_2$ in methyl alcohol	91.3	116.4
$CuCl_2$ in ethyl alcohol	(25.7)	(32.7)
$Ca(NO_3)_2$ in methyl alcohol	....	....
$Ca(NO_3)_2$ in ethyl alcohol	....	....
$CoCl_2$ in methyl alcohol	116.2	166.0
$CoCl_2$ in ethyl alcohol	31.6	(46.7)

Boiling-Point Data.

Table XLII.—Sodium Iodide in Methyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
53.949	2.8131	0.03478	0.429	12.33	46.8
55.352	2.7357	0.03300	0.425	12.90	53.6
61.195	2.5597	0.02790	0.3556	12.74	51.8
52.842	2.1082	0.02661	0.347	13.04	55.2
57.480	2.2060	0.02560	0.318	12.42	47.8
55.686	1.7227	0.02108	0.263	12.50	48.8
54.510	1.8380	0.02268	0.298	13.14	56.4
59.798	1.8080	0.02005	0.251	12.52	49.0
55.546	1.1943	0.01421	0.178	12.52	49.0
53.215	0.9665	0.01211	0.155	12.80	52.4

Table XLIII.—Sodium Iodide in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
53.100	3.1715	0.03984	0.585	14.63	27.7
54.734	2.7683	0.03374	0.512	15.17	31.9
64.744	3.2084	0.03303	0.495	14.98	30.2
53.896	2.6133	0.03235	0.481	14.87	29.3
61.293	2.5117	0.02730	0.402	14.73	28.0
55.509	2.0431	0.02455	0.365	14.86	29.1
61.701	2.1323	0.02306	0.351	15.22	32.3
59.294	1.9686	0.02214	0.327	14.76	28.3
54.368	1.5300	0.01877	0.281	14.97	30.1
64.926	1.4171	0.01455	0.223	15.32	33.2

Table XLIV.—Calcium Nitrate in Methyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
56.762	1.4954	0.01685	0.160	9.969	9.5
64.823	1.2154	0.01142	0.107	9.366	8.6
52.567	0.9792	0.01135	0.106	9.340	6.8
63.825	1.2489	0.01131	0.110	9.725	7.9
62.275	0.7453	0.00729	0.073	10.009	9.3

Table XLV.—Calcium Nitrate in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
50.476	1.1004	0.01328	12.68	0.168	5.1
54.301	1.3570	0.01228	12.86	1.158	5.9
52.355	0.6795	0.00791	12.51	0.099	4.4

Table XLVI.—Cadmium Iodide in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
48.831	3.5915	0.02007	0.253	12.60	4.8
54.657	3.6962	0.01850	0.230	12.43	4.05
50.956	3.1632	0.01694	0.214	12.63	4.9
51.574	2.9277	0.01549	0.195	12.58	4.7
52.348	2.7683	0.01443	0.181	12.57	4.6
52.316	2.6784	0.01397	0.176	12.58	4.6
48.034	2.1137	0.01201	0.152	12.67	5.0
51.668	1.2491	0.00660	0.082	12.42	4.0
56.563	0.8712	0.04204	0.052	12.38	4.3

DISCUSSION OF RESULTS.

Tables I to XVI show the conductivity of the various salts worked with in the pure solvents at both 0° and 25°. Nine of these tables show a maximum either at one or both temperatures. The other tables show no maximum up to the highest dilutions measured. In several cases maxima occur at one temperature and none at the other. In some tables the maxima occur at the same concentration at both temperatures; in others at different concentrations, but they always occur at concentrations which are close together. The temperature coefficients in general agree very well. Nearly all show a slight increase with increasing dilution.

Tables XVII to XXVIII show the conductivity of potassium iodide and cobalt chloride in mixtures of methyl alcohol and water at both 0° and 25°. In some of these tables the maximum conductivities are reached. The maxima generally occur at a greater concentration at 0° than at 25°. In a few tables the maxima occur at the same concentration at both temperatures. In nearly every case where there is a maximum there is a slight decrease in conductivity, then a rapid increase as dilution increases, thus giving an inflection in the curve.

Figs. II to IV give the curves for the conductivities of potas-

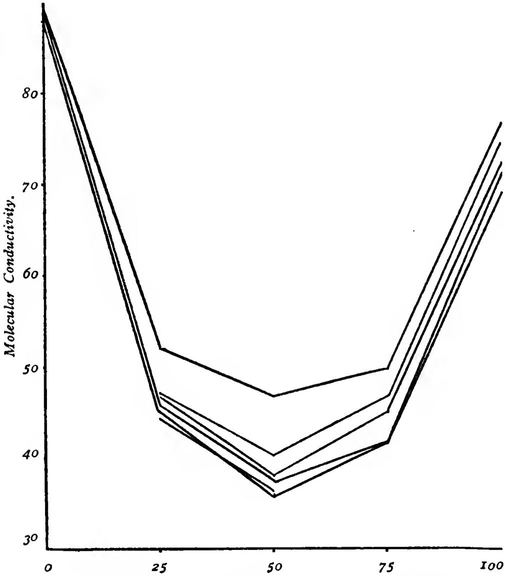

Fig. II.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 0°.

sium iodide in mixtures of methyl alcohol and water and of ethyl alcohol and water. The abscissas represent the percentage of alcohol and the ordinates represent the conductivity. In Fig. II there is a marked minimum with 50 per cent. methyl alcohol. Fig. III shows a minimum with 75 per cent. methyl alcohol. Fig. IV for potassium iodide in methyl alcohol-water mixtures shows the same characteristics. Fig.

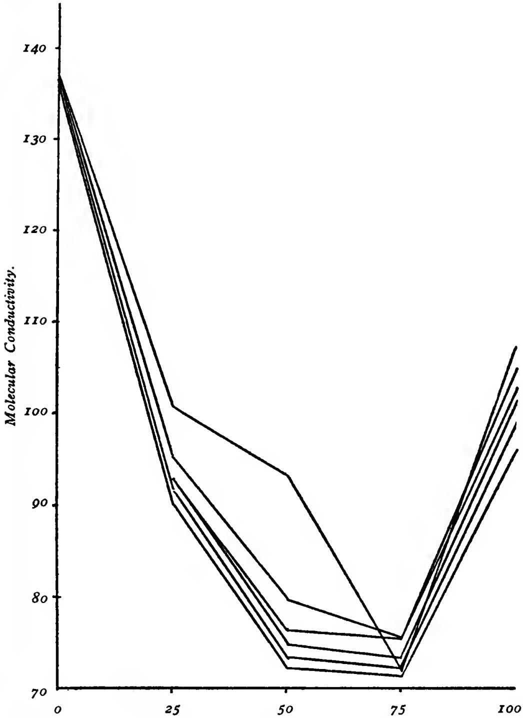

Fig. III.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 25°.

V shows a minimum for only three concentrations; these are with 75 per cent. ethyl alcohol.

Figs. VI to IX are the curves for the conductivity of cobalt chloride in methyl alcohol-water mixtures and ethyl alcohol-water mixtures at both 0° and 25°. Fig. VI shows a minimum with 50 per cent. methyl alcohol. Fig. VII shows minima in the curves with 75 per cent. methyl alcohol. In Figs. VIII and IX there is no minimum.

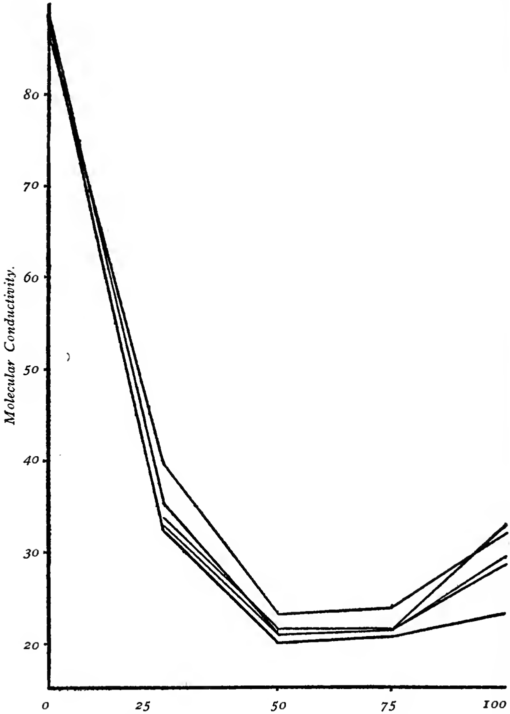

Fig. IV.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0°.

Tables XXIX to XXXVI represent the values for the conductivities of potassium iodide and cobalt chloride in mixed solvents, arranged according to temperature. The proportions in which the solvents are mixed and the concentrations vary. A study of the maxima of conductivity in these tables is interesting. The more probable values for μ_∞ are indicated by a (*). By means of these values we have calculated the dis-

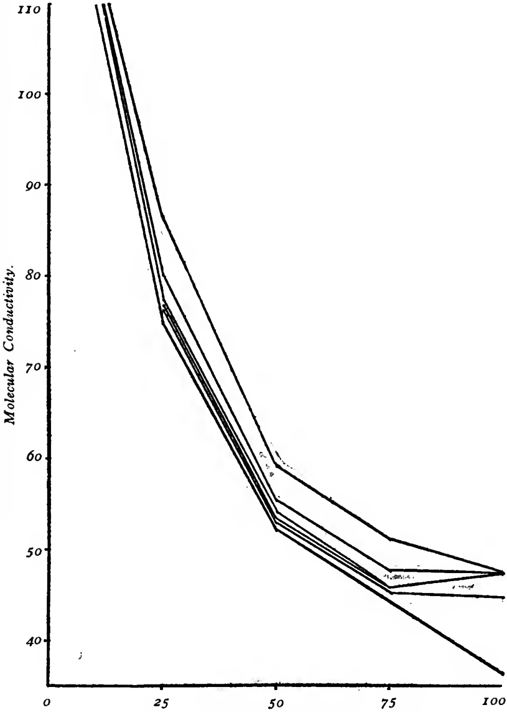

Fig. V.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 25°.

sociation of the salts at different volumes for four of these tables (XXIX, XXXI, XXXIII, and XXXV), since these present more μ_∞ values than the rest. We have used the well-known equation, $\alpha = \frac{\mu_v}{\mu_\infty}$ and the values for α are given in Tables XXXVII to XL. In Table XXXIII no μ_∞ occurs for 50 per cent. methyl alcohol-water mixtures.

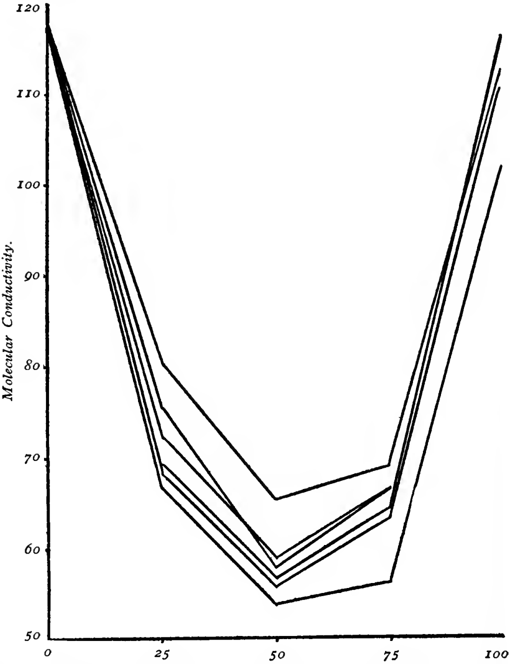

Fig. VI.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 0°.

These values for dissociation are interesting when compared with the values for the corresponding molecular conductivities. Fig. X gives the curves for dissociation corresponding to the molecular conductivity as indicated by the curves in Fig. IV. Fig. XI in the same manner corresponds to Fig. VI and Fig. XII to Fig. VIII.

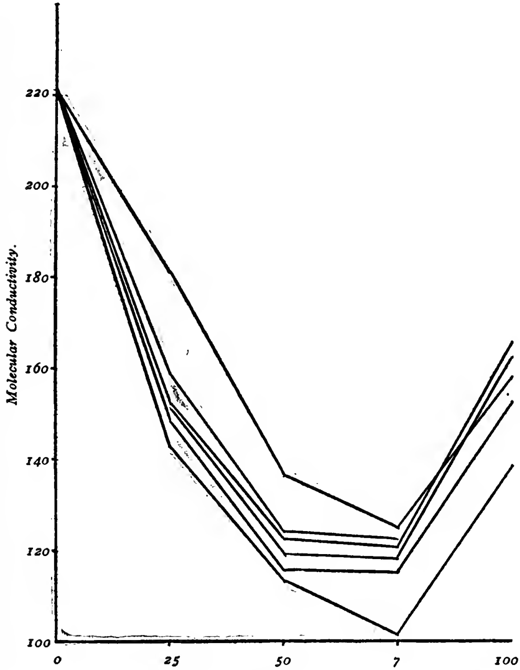

Fig. VII.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 25°.

In Fig. IV the conductivity curves of potassium iodide in ethyl alcohol-water mixtures at 0° show minima for all dilutions, while the corresponding curves for dissociation in Fig. X at first rise. If the equation $\alpha = \frac{\mu_v}{\mu}$ holds for mixed solvents this would indicate that at 0° the dissociation in 25 per cent. ethyl alcohol-water mixtures is slightly greater than in pure water. In all mixtures the dissociation is very much greater than it is in pure alcohol.

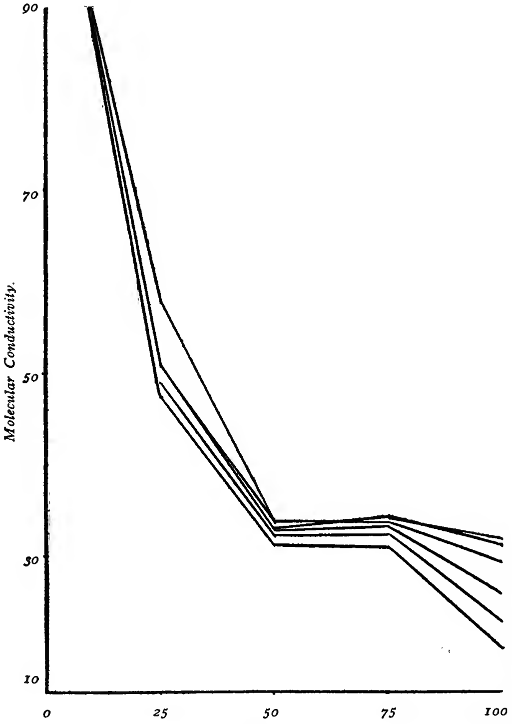

Fig. VIII.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 0°.

Fig. XI gives the curves for cobalt chloride in methyl alcohol-water mixtures corresponding to the molecular conductivity as represented by Fig. VI. The curves for dissociation show minima, but the drop below the straight line of averages is very small when compared with the large and decided minima in Fig. VI.

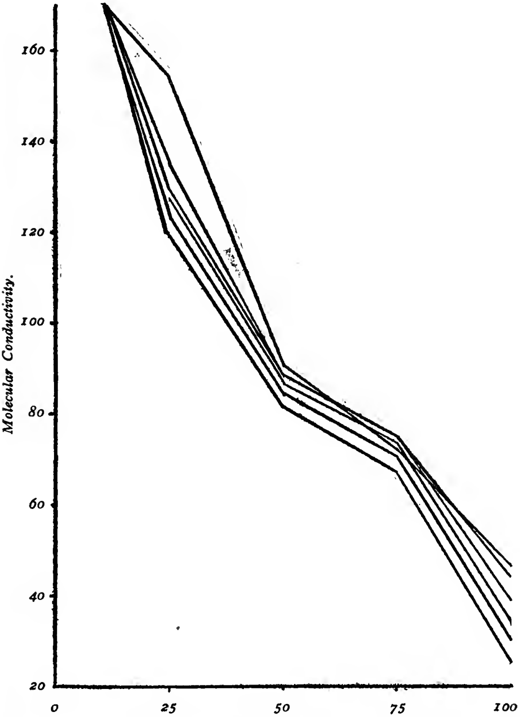

Fig. IX.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 25°.

Fig. XII for dissociation corresponds to Fig. VIII for molecular conductivity. The relation between these two figures is similar to the relation between X and IX. In both cases the mixed solvents are ethyl alcohol and water. In this case we have a binary salt, and the curves for Figs. X and XII are strikingly similar.

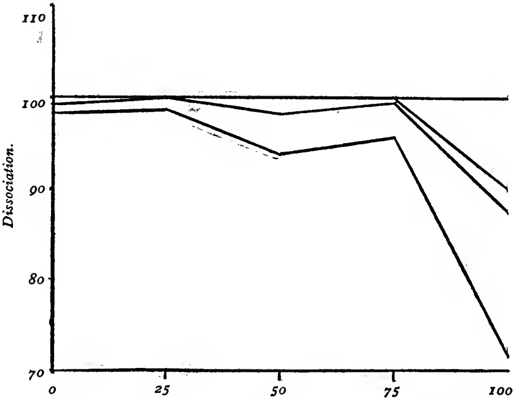

Fig. X.—Dissociation of potassium iodide in mixtures of ethyl alcohol and water at 0°.

The curves representing dissociation in ethyl alcohol-water mixtures are sometimes upward curves, taking a direction oppo-site to that of the curves representing conductivity, which are downward curves. This fact is especially apparent when Fig. IV,

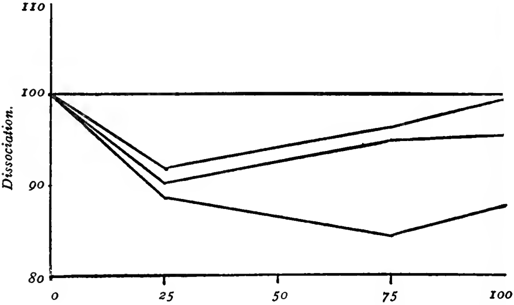

Fig. XI.—Dissociation of cobalt chloride in mixtures of methyl alcohol and water at 0°.

giving the curves for the conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0°, is compared with Fig. X, which gives the curves for the dissociation of these same solutions. This plainly indicates that the greatly diminished conductivity in mixed solvents is due not to diminished dissociation but to the other factor conditioning conductivity, *viz.*, diminished velocity of the ions through the solution. Though it had been previously pointed out that this diminished conductivity is due almost entirely to increased viscosity of the mixed solvent, it was not definitely known what the magnitude of the dissociation in these mixed solvents is, nor was it suspected that this dissociation might be greater in the mixed than in the pure solvents, as is shown to be the case by the curves for dissociation, some of these curves having maxima while those of conductivity have decided minima. These facts are quite marked where ethyl alcohol-water mixtures are used

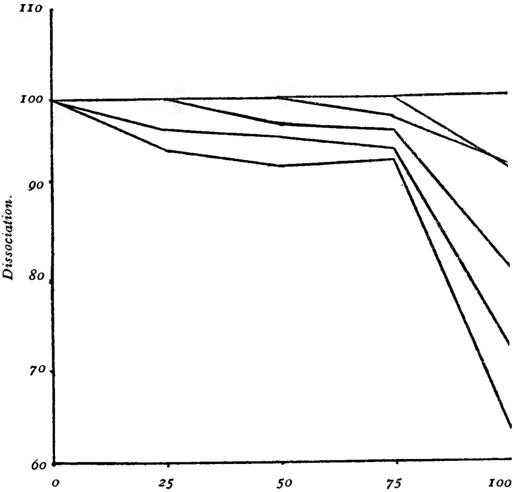

Fig. XII.—Dissociation of cobalt chloride in mixtures of ethyl alcohol and water at 0°.

as solvents. In such cases the increased viscosity, on the one hand, diminishes the conductivity, and the decreased dissociation, on the other, increases the conductivity. The viscosity in this case, since it is the more potent factor, causes the large minima in the curves for conductivity. These minima would be more marked than they are were it not for the slightly increased dissociation.

Table XLI gives the μ_∞ values of molecular conductivity for the various salts studied both in methyl and in ethyl alcohols at 0° and at 25°, whenever such values could be found. The values without the brackets were determined experimentally. Those within the brackets could not be determined experimentally because of the great dilutions and consequently unavoidable errors, but were calculated by a method given below.

An examination of the table reveals the fact that there is some relation between the maximum for each salt in the different solvents at any given temperature. It was suspected that this relation is a constant and that the following equation would hold:

$$\frac{\mu_\infty \text{ methyl}}{\mu_\infty \text{ ethyl}} = \text{constant}.$$

This equation was then applied with the following results:

Binary Electrolytes.

$LiNO_3$ at 0° = 2.37.
NaI 0° = 2.37.
NH_4Br 25° = 2.44.
NaI 25° = 2.17.

Ternary Electrolytes.

$CoCl_2$ at 0° = 3.68.

These facts make it appear probable that there is approximately such a constant for binary electrolytes and another for ternary electrolytes. These data are not sufficient, however, to give a final value to such constants. Further investigations will be required for this purpose. Most of these maxima occur at dilutions of $V = 12{,}800$ to $V = 51{,}200$. At these dilutions it is very difficult to obtain accurate results and the values for the constant are probably within the limits of experimental error.

The value for the constant between methyl and ethyl alcohols for binary electrolytes appears to be very nearly 2.37. We have obtained but one value for ternary electrolytes, which is 3.68. That is nearly 1.5×2.37. The latter value (3.56) is probably the more nearly correct. The factor 1.5 is employed since this expresses the ratio of ions present between binary and ternary electrolytes at complete dissociation.

With the data in hand we proceed to test further the accuracy of the above equation by supplying by calculation in Table XLI those μ_∞ values which could not be determined experimentally. The value of the constant was taken as 2.37 for binary electrolytes and 3.56 for ternary electrolytes. The calculated value for potassium iodide in methyl alcohol at 0° from the value in ethyl alcohol would be 77.5. An examination of Table I reveals the fact that this value is probably very nearly correct. For 25° it would be 112.6. Again from the same table this is probably correct. Ammonium bromide in ethyl alcohol at 0° would be equal to 30.3. This too as indicated by Table IV is probably nearly correct. Potassium sulphocyanate in methyl alcohol at 25° would have a value of 110.4. Table V indicates that this value is probably correct within the limits of experimental error. Lithium nitrate gives a value of 96.7 in methyl alcohol at 25°; compared with Table VII this would seem to be nearly correct.

With ternary electrolytes there are only three cases to which this equation can be applied. Copper chloride in ethyl alcohol at 0° would give a value of 24.8, and cobalt chloride in ethyl alcohol at 25° would give 46.7 as the value for the maximum in conductivity. In Table XIV, at 0°, a maximum is reached at $V = 25600$. The maxima at the different temperatures as a rule do not occur very far apart. We believe that the value 46.7 is pretty nearly correct for the maximum for cobalt chloride in ethyl alcohol at 25°. The only two values which do not fit into the table are the value for potassium cyanide in methyl alcohol at 0° and that for copper chloride in ethyl alcohol at 25°. The latter, however, is not far from what we might expect it to be.

We believe from the above results that the ratio between the maxima in molecular conductivity for different salts in methyl alcohol and the maxima for the same salts in ethyl alcohol is probably constant for all binary electrolytes, that for all ternary electrolytes it is a constant of different value, and that there is a definite relation between these two constants.

Jones, in an article on "The Electrolytic Dissociation of Certain Salts in Methyl and Ethyl Alcohols, as Measured by the Boiling-Point Method," gives the following table which expresses "the dissociation values of the above alcohols as calculated from data obtained by the boiling-point method." The ratios of these values were calculated and are also expressed in the table:

Table XLVII.

Substance.	Dilution normal.	Dissociation in methyl alcohol. Per cent.	Dissociation in ethyl alcohol. Per cent.	Ratio.
KI	0.1	52	25	2.08
NaI	0.1	60	33	1.8
NaBr	0.1	60	24	2.5
NH_4Br	0.2	49	21	2.3
CH_3COOK	0.1	36	16	2.3
CH_3COONa	0.1	38	14	2.7
$Ca(NO_3)_2$	0.1	15	5	3.0

Leaving out the value 1.8 for sodium iodide, which is evidently erroneous, we obtain as a mean from the other values of the binary electrolytes 2.37 which, it will be remembered, is the same as the value obtained above by the conductivity method for the ratio between the maxima in the different alcohols. The value in this table for the one ternary electrolyte is not so great as that determined by the conductivity method, and yet it is possible that more data would give comparable values.

The boiling-point data in this work were obtained by means of the boiling-point apparatus used by Jones.[1] Both solvents were carefully purified and dried.

Table XLIV gives the dissociation of certain salts as calculated by both the conductivity and boiling-point methods:

Table XLIV.

Salt.	Solvent.	Dissociation from conductivity method. Per cent.	Dissociation from boiling-point method. Per cent.
KI	Methyl	65	49
KI	Ethyl	49	26
NaI	Methyl	75	61
NH_4Br	Methyl	71	47
NH_4Br	Ethyl	40	20

It will be seen at a glance from the above table that the dissociation values as determined by conductivity are higher than those found by the boiling-point method, in both methyl and ethyl alcohols. This may possibly be due to a polymerization of the undissociated molecules in the solvent in question. This would give too low dissociation as measured by the boiling-point method, since this method takes into account both the molecules and the ions, while the conductivity method deals only with the ions.

SUMMARY.

We have measured the conductivity of various salts in pure methyl and ethyl alcohols at very high dilutions, and also in mixtures of methyl and ethyl alcohols with water. In many of these measurements we have found the value of μ_∞.

Many of these values were found to occur at concentrations between $V = 3200$ and $V = 51200$.

A constant ratio was found between the values of μ_∞ for several binary electrolytes in methyl alcohol and in ethyl alcohol, and the ratio for one ternary electrolyte was worked out. These facts indicate that there is a definite relation between these two ratios.

We have found minima in most of the curves for mixed solvents.

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[1] Z. physik. Chem., **31**, 114 (1899) (Jubelband zu van't Hoff).

We have tabulated the dissociation of several salts in methyl alcohol and ethyl alcohol as determined by the boiling-point method.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June 1910.

REVIEWS.

THE VEGETABLE PROTEINS. By THOMAS B. OSBORNE, PH.D., Research Chemist in the Connecticut Agricultural Experiment Station, New Haven, Connecticut. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. xiii + 125.

This work forms one of the series of excellent monographs on biochemical subjects appearing under the editorship of Messrs. Hopkins and Plimmer. The editors are to be congratulated upon securing the services of Dr. Osborne for writing the section devoted to the vegetable proteins. Dr. Osborne has contributed so largely to the investigation of the vegetable proteins by precise chemical methods that most of the questions discussed in the present volume are based upon his own investigations. The writer has wisely thought it more important to discuss the general physical and chemical properties of the vegetable proteins rather than to give a detailed descriptive account of the individual substances.

A chapter in which the subjects of toxalbumins, anaphalaxis and related topics are lightly touched upon in so far as they relate to the vegetable proteins forms the concluding section of a truly admirable monograph. W. D. DAKIN.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS, Volumes II and III. Fourth edition. Philadelphia: P. Blakiston's Son & Co. 1910. pp. x + 520 and x + 635. Price, $5.00 per volume.

These two volumes cover the ground of Parts I and II and a portion of Part III of volume II of the third edition and show an increase of about 300 pages in the text devoted to the subjects covered.

Volume II is edited by Henry Leffmann and W. A. Davis, Volume III by W. A. Davis and Samuel S. Sadtler. In both cases a number of authors have contributed to the revision of the text, the sections and authors being as follows: Volume II, Fixed oils, fats and waxes (Mitchell); Special characters and Methods (Archbutt); Butter fat (Revis and Bolton); Lard (Mitchell); Linseed oil (Klein); Higher fatty acids (Robertson); Soap (Leffmann); Glycerol (Davis); Cholesterols (Gardner); Wool fat, cloth oils (Gill). Volume III, Hydrocarbons (Garrett); Bitumens (Sadtler); Naphthalene and its derivatives (Davis); Anthracene and its associates (Sadtler); Phenols (Sadtler); Aromatic acids (Horton); Gallic acid and its allies (Dreaper); Phthalic acids and the phthaleins (Davis); Modern explosives (Marshall).

As in earlier editions, many sections consist as largely of descriptive material as of analytical methods. In some of the sections the treatment follows that of the third edition so closely as to suggest that the revision was here accomplished by piece-meal insertions rather than by a thorough rewriting. As a rule, however, close examination shows numerous inconspicuous changes in older portions of the text and makes it appear that the revisers have done their work conscientiously but sometimes too conservatively. In some cases material which is now rather antiquated is retained in full while the newer work on the same topic is given very incompletely. On the other hand, no part of the work is wholly lacking in modern material and recent references and certain sections have been thoroughly revised and brought well up to date.

The descriptions of individual oils, fats and waxes, which occupy a large part of Volume II, are of great value. This part of the text has been more than doubled in extent and now covers about 300 pages.

In view of the paucity of convenient literature on American petroleum it is fortunate that the section on Bitumens (which includes petroleum and its products) has been expanded at least one-third, largely by the introduction of American material.

In the section on Phenols considerable attention is appropriately given to the subject of the examination of creosote oils for timber preservation.

In printing and binding this edition is a decided improvement over the last and there are not many typographical errors, but some obviously incorrect data were noted in Volume II (*viz.*, for the saponification number and saponification equivalent of linolein on page 17, and the flashing point of linseed oil attributed to Rakusin on page 331) and the headings and placing of new material are not always in harmony with the classification of the old. Partly for this reason and partly because the work is likely to be used more for reference than for consecutive reading a more detailed index might be advantageous.

The work as a whole is to be heartily welcomed. Since certain large fields of organic analysis are now so well covered by special reference books, this new edition of Allen cannot be expected to occupy the unique position which was held in its day by the original treatise, but it is one of the works which should be at the hand of every chemist who has to do with the analysis of either natural or manufactured organic materials. H. C. S.

THE YEAR-BOOK FOR COLORISTS AND DYERS, Presenting a Review of the Year's Advances in the Bleaching, Dyeing, Printing and Finishing of Textiles. By HERMANN A. METZ. Volume XII. New York: Hermann A. Metz, 122 Hudson Street. 1909. pp. 388.

The volume contains reference tables, patents for the year 1909, notes on processes, new colors, etc., a long list of dyestuffs with the name of the maker, and reference to dyeing methods in addition to miscellaneous matter. The volume is, without doubt, useful to dyers and textile chemists. The list of schools giving courses in textile chemistry or dyeing is by no means complete. One has no right, however, to expect this in works of this kind. G. S. F.

IDENTIFICATION OF THE COMMERCIAL DYE-STUFFS, Being Vol. III of a Method for the Identification of Pure Organic Compounds by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions. Containing Classified Original Descriptions of Nearly 1700 Synthetic and Natural Dye-Stuffs; References to Many Allied Brands; Suggestions on the Examination of Dye-Stuffs in Mixtures; and a Color Standard. BY SAMUEL PARSONS MULLIKEN, PH.D., Assistant Professor of Organic Chemical Research at the Massachusetts Institute of Technology, Boston, Mass. New York: John Wiley & Sons; London: Chapman and Hall, Limited. 1910. pp. vi + 274. Price, $5.00.

This book contains original descriptions of nearly 1700 dye stuffs, and is intended to provide for their identification, chiefly in the powder or paste form. The dye stuffs are first tested for homogeneity, divided into groups according to their behavior towards textiles, and to their other properties, and then identified by means of further tests. The entire process appears to be long and tedious, but the exact identification of one out of seventeen hundred dye stuffs cannot well be a rapid process. No doubt dye stuff chemists have shorter tests and methods, which are, however, based upon their knowledge and experience as to colors and appearances and are difficult to reduce to writing. Dr. Mulliken's book has the appearance of a very tedious piece of work, well done, and will no doubt be useful to those who need to identify dyestuffs.

G. S. F.

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THE HYDROLYSIS OF ACID AMIDES.

BY E. EMMET REID.

The work[1] here reported was done two years ago in coöperation with the extensive investigations of Professor Acree and his coworkers on catalysis.[2] Though the conductivity side of the work still remains to be done, yet since I do not intend to continue the work from this point of view, it seems best to publish what has been done so far, so as to leave the way clear for the continuation of the work in other hands.

Acree and Nirdlinger,[3] working with acetamide and using hydrochloric acid as catalyst, found that the molecular reaction velocity varied considerably, both with the concentration of the amide and with that of the catalyst, the variation in both cases being in the direction, and of the magnitude, which was predicted from conductivity studies of the various solutions on the assumption which they made, that the reacting substance is a complex ion (or salt) formed by union of the hydrogen ion (or both ions) with the amide. This observation confirmed their belief in the analogy of the hydrolysis of acid amides to the formation of ethers and esters by the action of alkyl (acyl) halides on the salts of alcohols, phenols, urazoles,[4]

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[1] This work was aided by a grant from the Carnegie Institution of Washington to S. F. Acree.

[2] THIS JOURNAL, **28,** 370; **37,** 71, 410; **38,** 258, 489, 746 **39,** 145, 226, 300. J. Am. Chem. Soc., **30,** 1755. Ber. d. chem. Ges., **41,** 3199.

[3] THIS JOURNAL, **38,** 489.

[4] Ber. d. chem. Ges., **41,** 3199. Also earlier and more recent papers.

etc., to esterification and the inversion of cane sugar as worked out by Bredig,[1] Goldschmidt, Kastle, and Acree and Johnson,[2] to the formation and hydrolysis of oximes, as shown by Lapworth and Barrett[3] and by Acree and Johnson[4] and Deshea,[5] and to the decomposition of imido esters as studied by Stieglitz.[6]

The present work was undertaken to test this theory more thoroughly by studying several amides at widely different concentrations both of amide and of catalyst. The amides used were benzamide and acetamide with barium hydroxide as catalyst. All of the work was done at 25°, so as to be more readily coördinated with existing conductivity data, as well as to facilitate the making of such additional conductivity measurements as might be required.

Materials.—The benzamide was recrystallized several times from water, once from dilute ammonia, once from alcohol, and finally from conductivity water. The acetamide was distilled several times and recrystallized from acetone. The barium hydroxide was recrystallized. Conductivity water of high purity was used in making and diluting all solutions on which measurements were to be made. Redistilled ammonia-free water was used in filling the distillation flasks.

Work with Benzamide.

Method of Work.—The reactions were carried on in Erlenmeyer flasks, of 120 cc. capacity, of "Nonsol" glass. Before use, they were heated for several days with dilute hydrochloric acid. The rubber stoppers used and the small tubes placed in the flasks were also well boiled out. The benzamide for an experiment was weighed into the flask, the proper amount of barium hydroxide solution and of pure water run in to make the desired strength of solution, the stopper inserted, and the flask gently shaken till all of the benzamide had gone into solu-

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[1] Z. Elek. Chem., **9,** 118, **10,** 585, 586; **11,** 528.

[2] THIS JOURNAL, **38,** 258. This article contains full references to many important articles on reaction mechanisms.

[3] J. Chem. Soc., **91,** 1133; **93,** 85.

[4] THIS JOURNAL, **38,** 308; **39,** 300.

[5] Dissertation, Johns Hopkins University, 1909.

[6] Report International Congress of Arts and Sciences, St. Louis, **4,** 276. THIS JOURNAL, **39,** 29, 126, 402, 437, 586, 719.

tion. The slight solubility of benzamide at 25° caused much trouble. In order to lessen the danger of loss of ammonia from the alkaline solution, a tube 18 by 60 mm., closed at one end, and containing enough dilute hydrochloric acid to absorb the ammonia likely to be given off during the reaction, was stood up in the flask before inserting the stopper. In order to prevent mixing of the solutions by crawling, the upper portion of the tube was coated with purified paraffin. The flask containing the reacting mixture was sunk to the neck in a water bath heated by electricity as described by Morse and Holland.[1] The temperature was kept constant to within about 0°.01. To stop the reaction, 5 cc. of a 5 normal magnesium chloride solution was run in.

Method of Analysis.[2]—The reaction mixture and the contents of the tube containing the acid were washed into a flask and distilled with steam for 70 minutes with magnesium hydroxide. The percentage of decomposition thus found was corrected for the amount of the remaining benzamide hydrolyzed during the distillation by subtracting 0.21 per cent. of $(100 - x)$ from x, where x is the percentage of decomposition found.[3]

Results.—Table I gives the results of experiments in which the concentration of the barium hydroxide was kept constant and that of the benzamide was varied from 0.015 to 0.060 normal. The time is given in days. The results are calculated by means of the usual formula for a reaction of the second order, A being the concentration of the barium hydroxide and B that of the benzamide. The upper half of the table gives the analytical data in percentage of decomposition found, and the lower half gives the values of K, the reaction velocity, calculated from these data. A few values of K which are out of harmony with the others in the series are given in parentheses and were not used in making the averages. In column 1, the amount of benzamide used was 0.1681 gram to 100 cc. of solution, while in the others

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[1] This Journal, **41**, 92.

[2] *Ibid.*, **21**, 293.

[3] *Ibid.*, **41**, 486.

the amount of benzamide was 0.3363 gram, or 3 millimoles, to 100, 75 and 50 cc. of the barium hydroxide.

Table I.

A	0.3489	0.3489	0.3489	0.3489
B	0.015	0.030	0.040	0.060
A–B	0.3339	0.3189	0.3089	0.2889
A/B	23.26	11.63	8.722	5.815
		Percentage of Hydrolysis.		
1 day	33.96	32.75	32.49	31.53
2 days	55.51	53.55	52.77	51.06
3 days	70.30	68.20	66.58	66.09
4 days	79.33	78.60	77.03	73.98
6 days	91.24	.....	88.44	86.24
7 days	93.40	90.97	91.50	86.41
		Velocity Constants.		
1 day	1.171	1.155	(1.149)	1.118
2 days	1.177	1.132	1.113	1.082
3 days	1.182	1.134	1.111	1.108
4 days	(1.154)	1.154	1.116	1.048
6 days	1.181	.....	1.094	1.025
7 days	1.145	1.041	1.099	(0.907)
Average	1.171	1.118	1.107	1.075

The results show that the reaction proceeds regularly till at least 90 per cent. of the benzamide is used up.

Table II gives the results of experiments in which the concentration of the amide was kept constant and that of the barium hydroxide was varied. The amount of benzamide was 0.3363 gram and the volume was 75 cc. The values in column 1 are taken from column 3 of Table I.

Table II.

A	0.3489	0.30	0.20	0.10
B	0.040	0.40	0.04	0.04
A–B	0.3089	0.25	0.16	0.06
A/B	8.722	7.50	5.00	2.50
		Percentage of Hydrolysis.		
1 day	32.49	27.35	.....	.....
2 days	52.77	.....	30.62	14.97
3 days	66.58	60.31	42.60	22.22
4 days	77.03	71.02	51.31	27.43

Velocity Constants.

1 day	(1.149)	1.086	.....	.....
2 days	1.113	.....	0.945	0.837
3 days	1.111	1.077	0.970	0.878
4 days	1.116	1.097	0.955	0.852
Average	1.118	1.087	0.963	0.865

Acetamide.

The following work with acetamide was intended to parallel that with benzamide in a general way. Owing to the greater reactivity of acetamide, the time periods are much shorter and hours take the place of days in the table. On account of its greater solubility considerably greater concentrations of amide could be used. The concentrations of the barium hydroxide were the same, with the addition of one 0.05 normal. The results are not satisfactory though much work was put upon them. The small molecular weight of acetamide makes rather accurate weighings necessary, but acetamide is very hygroscopic and gains rapidly in weight during the weighing, the gain varying according to the weather. In some of the experiments a 0.3 normal stock solution was made up and 10 cc. of this measured into each flask. However, it was found that such a solution, even when made up with conductivity water, is hydrolyzed appreciably in a day or two, so that fresh solutions had to be prepared for each day's work. The acetamide was crystallized from acetone and was kept in a desiccator all the time. It must have occluded some of the solvent or have failed to dry in the desiccator since equal weighed samples gave irregular amounts of ammonia on distillation with sodium hydroxide. A further cause of uncertainty in the results is that the amount of acetamide decomposed by boiling with magnesium hydroxide is considerable, amounting to 0.4 per cent. on the average, but seeming to be somewhat irregular as judged from a number of blank experiments.

In Table III are given results of experiments with barium hydroxide of constant concentration and acetamide of six concentrations from 0.03 up to 0.30 normal, that is, with 0.1772 gram of acetamide in 100, 75, 50, 25, 15 and 10 cc.

of the barium hydroxide solution. The amide was weighed into each of the flasks or tubes. For the three larger volumes, flasks were used exactly as described for benzamide, but for the smaller volumes, i. e., 25, 15 and 10 cc., test tubes were employed. These had previously been drawn down to a neck and were sealed off immediately after putting in the solution.

In the analysis of the reaction mixtures the ammonia was first determined by distillation with magnesium hydroxide in the usual way and then, after putting on another receiver, excess of strong sodium hydroxide solution was run in and the distillation continued for an hour longer. This decomposed the acetamide present and drove over most of the resulting ammonia. After an hour's distillation with the caustic soda, the receiver was removed and an empty flask put in its place and the distillation continued for one hour more. The ammonia thus obtained was usually equivalent to between 0.04 and 0.10 cc. of tenth-normal acid. Since 3 millimoles of acetamide was used, which should give ammonia equivalent to 30 cc. of tenth-normal acid, the three amounts of ammonia found should, when added together, equal this amount. The standard acid used was of such strength that the amount neutralized should have been 30.06 instead of 30 cc.

In the first part of the table are given the concentrations, etc., in the next part the amounts of standard acid neutralized in the three distillations of each sample, then the percentage of decomposition corrected for the amount of amide decomposed by the magnesium hydroxide, and finally, in the lower portion, the velocity constants calculated from these percentages. It will be noted that the amounts of acid neutralized seldom add up to 30.06 cc., the calculated amount. This is likely due to several causes: the amide may have contained irregular amounts of water as mentioned above, or some ammonia may have been lost either from the flasks in the long-time periods or during the transfer of the reaction mixtures to the distilling flasks. To avoid leakage the stoppers were inserted as tightly as practicable in the reaction flasks, and to avoid loss of ammonia during the transfer, the reaction mixtures were made as nearly neutral as possible immediately after stopping the reaction. Besides, there may have been some loss during distillation, and there are always errors in the titration of large volumes of liquids and these, of course, added in some cases and cancelled in others. The percentage of decomposition is calculated in each case from the total ammonia actually found rather than from the amount calculated.

A is the concentration of the barium hydroxide and *B* that of the acetamide. The time is given in hours.

Table III.—Acetamide.

A	0.3489	0.3489	0.3489	0.3489	0.3489	0.3489
B	0.03	0.04	0.06	0.12	0.20	0.30
A–B	0.3189	0.3089	0.2889	0.2289	0.1489	0.0489
A/B	11.67	8.722	5.815	2.907	1.744	1.163
Volume	100	75	50	25	15	10

Titrations.

5 hours	6.79	6.74	6.66	6.52	6.22	6.01
	22.95	22.99	23.27	23.36	23.74	23.96
	0.09	0.11	0.04	0.06	0.01	0.04
	29.83	29.84	29.97	29.94	29.97	30 01
15 hours	15.48	15.30	15.17	14.66	13.61	12.82
	14.30	14.36	14.52	15.25	16.31	17.11
	0.10	0.10	0.05	0.05	0.04	0.03
	29.88	29.76	29.74	29.96	29.96	29.96
20 hours	19.66	19.27	18.92	18.26	17.12	15.67
	10.30	10.43	10.72	11.57	12.73	14.18
	0.10	0.09	0.02	0.02	0.02	0.04
	30.06	29.79	29.66	29.85	29.87	29.89
40 hours	25.39	25.23	25.27	24.35	22.67	20.70
	4.18	4.22	4.52	5.57	7.14	9.14
	0.09	0.09	0.05	0.07	0.00	0.03
	29.66	29.34	29.84	29.99	29.81	29.87

70 hours	28.73	28.52	.....	27.69	26.28	23.80
	1.07	1.25	.....	1.97	3.39	5.67
	0.05	0.09	.....	0.02	0.04	0.04
	29.85	29.86	.....	29.68	29.71	29.51

Corrected Percentages of Hydrolysis.

5 hours	22.45	22.28	21.91	21.46	20.43	19.71
15 hours	51.61	51.21	50.81	48.73	45.21	42.56
20 hours	65.32	64.41	63.71	61.08	57.22	52.44
40 hours	85.57	85.56	84.65	81.15	76.00	69.24
70 hours	96.23	95.49	.....	93.27	88.40	80.58

Velocity Constants.

5 hours	0.1472	0.1465	0.1446	0.1440	0.1405	0.1383
15 hours	0.1422	0.1418	0.1426	0.1411	0.1359	0.1347
20 hours	0.1570	0.1548	0.1553	0.1546	0.1525	0.1469
40 hours	0.1458	0.1483	0.1486	0.1465	0.1444	0.1402
70 hours	[illegible]	0.1380	[0.1420]	0.1442	0.1381	0.1272
Average	0.1470	0.1459	0.1471	0.1461	0.1427	0.1374

The value in brackets was supplied from adjacent values so as to balance the different time periods in the general averages. In these experiments, as in the ones that follow, all the samples for the same time period were in the bath together so that any fluctuation of the temperature affected all alike. In the 20-hour experiments the temperature was too high for a part of the time. The purpose of the experiments was to find the influence of the concentration of the amide on the velocity, and this influence is broguht out in this table in spite of its imperfections. The work was, however, repeated and somewhat enlarged and the results are given in Table IV, which follows. The fact that the total ammonia found in the titrations is larger is partly due to expansion of the standard solutions in warmer weather. The concentration of amide varied, the base remaining constant.

Table IV.—Original Concentrations.

A	0.3489	0.3489	0.3489	0.3489	0.3489	0.3489
B	0.03	0.04	0.06	0.12	0.20	0.30
A–B	0.3189	0.3089	0.2889	0.2289	0.1489	0.0489
A/B	11.67	8.722	5.815	2.907	1.744	1.163
Volume	100	75	50	25	15	10

Titrations.

2.5 hours	3.59	3.56	3.64	3.55	3.22	3.22
	25.94	26.17	26.21	26.37	26 33	26.10
	0.07	0.11	0.05	0.04	0.02	0.06
	29.60	29.34	29.90	29.96	29.56	29.38
5 hours	6.90	6.43	6.60	6.45	6.33	5.75
	22.96	22.41	23.27	23.40	23.44	23.62
	0.18	0.17	0.08	0.05	0.04	0.05
	30.04	29.01	29.95	29.90	29.82	29.42
10 hours	11.74	11.55	11.51	11.14	.....	10.01
	18.31	18.48	18.44	18.98	.....	20.01
	0.09	0.09	0.08	0.06	.....	0.02
	30.14	30.12	30.03	30.20	.....	30.04
15 hours	15.61	.....	15.38	14.74	13.83	12.31
	14.25	14.45	14.68	15.30	15.99	16.99
	0.09	0.09	0.06	0.06	0.02	0.04
	29.95	.....	30.12	30.10	29.84	29.34
20 hours	18.53	18.32	18.35	17.43	16.49	15.12
	11.39	11.41	11.74	12.57	13.59	14.75
	0.12	0.14	0.06	0.08	0.05	0.03
	30.04	29.87	30.15	30.08	30.13	29.90
30 hours	22.78	22.71	22.36	21.34	19.93	18.20
	7.12	7.36	7.64	8.79	10.03	11.73
	0.12	0.10	0.06	0.04	0.06	0.04
	30.02	30.17	30.06	30.17	30.02	29.97
50 hours	27.11	26.88	26.62	25.61	24.18	.....
	2.91	3.01	3.32	4.24	5.83	
	0.09	0.10	0.05	0.04	0.05	
	30.11	29.99	29.99	29.89	30.06	.....

70 hours	28.73	28.56	28.41	27.71	26.28	24.03
	1.29	1.29	1.46	2.25	3.61	5.76
	0.06	0.08	0.02	0.05	0.04	0.05
	30.08	29.93	29.89	30.01	29.93	29.84

Corrected Percentages of Hydrolysis.

2.5 hours	11.84	11.61	11.85	11.53	10.57	10.64
5 hours	22.69	21.88	21.76	21.29	20.95	19.25
10 hours	38.88	38.16	38.04	36.69	.....	33.09
15 hours	51.95	.....	50.88	48.78	46.16	41.76
20 hours	61.55	61.19	60.71	57.80	54.56	50.39
30 hours	75.77	75.18	74.29	70.63	66.27	60.59
50 hours	90.01	89.59	88.72	85.63	80.37	.....
70 hours	95.50	95.40	95.03	92.32	87.76	80.53

Velocity Constants.

							Average.
2.5 hrs.	0.1440	0.1424	(0.1461)	0.1433	0.1425	0.1355	0.1415
5 hrs.	0.1437	0.1410	0.1434	0.1427	0.1437	0.1341	0.1419
10 hrs.	0.1437	0.1411	0.1427	0.1407	[0.1414]	0.1371	0.1411
15 hrs.	0.1437	0.1428	0.1429	0.1413	0.1404	(0.1305)	0.1403
20 hrs.	0.1413	0.1414	0.1426	0.1409	0.1372	0.1360	0.1401
30 hrs.	0.1411	0.1407	0.1409	0.1380	0.1372	0.1328	0.1385
50 hrs.	0.1395	0.1394	0.1398	0.1391	0.1365	......	0.1389
70 hrs.	0.1354	0.1370	0.1396	0.1362	0.1350	0.1333	0.1360
Average,	0.1416	0.1407	0.1417	0.1403	0.1392	0.1348	......

The value in brackets is supplied by interpolation.

The next question taken up was the effect of changes in the concentration of the barium hydroxide and of the presence of neutral salts on the velocity of the reaction, the concentration of the acetamide being kept constant. The results of these experiments are given in Tables V and VI, of which V is merely preliminary. The volume of the reaction mixture was in all cases 75 cc. In Table VI, the values for the 0.3489 N base are taken from Table IV for the same concentration of the amide. For the experiments with addition of barium chloride, the barium salt as well as the amide were weighed into the flask for each experiment, but for the other experiments, 10 cc. of a 0.3 normal solution of the amide was measured out each time and the calculated amount of the strong barium hydroxide solution and of conductivity water added to make the required strength of solution. The acetamide solution was made up just before using. The six samples for the same time period were always in the bath at the same time so that any variation in temperature could not affect the relative values. Since all the samples in a set contained the same original amount of amide, only one distillation was made in the analysis of the reaction mixture. The results for the 0.3489 normal base and for this plus 1 normal barium chloride are not strictly comparable since in these the amide was weighed for each experiment instead of being measured out from a stock solution, and in the former the percentage was calculated from the total ammonia actually found rather than from the weight of the amide.

Table V.

Original Concentrations.

A	0.30	0.20	0.10
B	0.04	0.04	0.04
A–B	0.26	0.16	0.06
A/B	7.5	5.0	2.5

Percentages of Hydrolysis, Corrected.

5 hours	19.33	13.05	6.50
20 hours	55.17	40.99	22.97
72 hours	93.75	83.38	57.65

Velocity Constants.

5 hours	0.1452	0.1417	0.1362
20 hours	0.1396	0.1381	0.1372
72 hours	0.1410	0.1400	0.1382
Average	0.1419	0.1399	0.1372

Table VI.

Original Concentrations, etc.

A	0.3489	0.3489 $+BaCl_2$	0.30 $+Ba(C_2H_3O_2)_2$	0.30	0.20	0.10	0.05
B	0.04	0.04	0.04	0.04	0.04	0.04	0.04
A–B	0.3089	0.3089	0.26	0.26	0.16	0.06	0.01
A/B	8.722	8.722	7.50	7.50	5.00	2.50	1.25

Percentages of Hydrolysis, Corrected.

2.5 hrs.	11.64	11.55	9.25	10.42	7.07	3.50	1.73
5 hrs.	22.88	21.57	17.84	19.50	12.59	6.67	3.16
10 hrs.	38.16	37.53	22.31	34.00	23.75	12.71	6.66
15 hrs.	.....	50.73	44.56	46.40	33.24	18.57	9.70
20 hrs.	61.19	61.07	53.78	55.99	41.43	23.42	12.70
30 hrs.	75.18	71.41	67.93	70.61	54.38	32.10	17.52
50 hrs.	89.59	88.40	82.99	85.94	72.12	46.32	26.69
70 hrs.	95.40	94.07	91.09	92.40	81.40	56.04	33.50

Velocity Constants.

2.5 hrs.	0.1424	0.1416	0.1385	0.1477	0.1476	0.1435	0.141
5 hrs.	0.1410	0.1412	0.1327	0.1419	(0.1354)	0.1372	(0.130
10 hrs.	0.1411	0.1380	0.1331	0.1420	0.1390	0.1396	0.141
15 hrs.	0.1428	0.1398	0.1355	0.1436	0.1400	0.1422	0.141
20 hrs.	0.1414	0.1410	0.1341	0.1429	0.1401	0.1403	0.143
30 hrs.	0.1407	(0.1259)	0.1336	0.1444	0.1395	0.1387	0.138
50 hrs.	0.1394	(0.1325)	(0.1273)	0.1415	0.1402	0.1391	0.138
70 hrs.	(0.1370)	(0.1254)	(0.1258)	(0.1343)	(0.1343)	(0.1352)	0.137
Aver.	0.1415	0.1400	0.1338	0.1427	0.1398	0.1400	0.140

In making up the averages, the values in parentheses are left out as being out of harmony with adjacent values, as are also those for the 2.5-hour time period. In these short-period experiments, particularly with the lower concentrations of base, the amount of ammonia found is very small and the correction for acetamide decomposed during the distillation with magnesium hydroxide is comparatively large, and the results are therefore uncertain. In the very long time periods there is greater danger of loss of ammonia, disturbing influences due to the change of the medium, etc., have a greater opportunity to affect the results, and the reaction being so nearly complete, the change per hour is extremely slow and consequently unavoidable analytical errors influence the results unduly. In the higher concentrations, at the end of 70 hours the reaction is progressing at the rate of only 0.2 per cent. per hour. For this reason, values for time periods of over 30 hours were not used in making up the averages for the highest concentration.

Hydrolysis of Acetamide in Pure Water.

One of the solutions, which, after standing several days, showed slight hydrolysis, was examined microscopically and appeared to contain bacteria, but of what kind they were or whether they were in any way connected with the hydrolysis was not determined. Two of these 0.3 normal solutions of acetamide stood about 18 months in clean glass-stoppered bottles without being opened in the interval. On analysis, one showed 23.2 and the other 55.2 per cent. hydrolysis.

DISCUSSION OF RESULTS.

Change of Velocity with Change of Concentration of the Amide.

In Table VII, the average velocities for benzamide are taken from Table I and those for acetamide from Table IV, the latter being multiplied by 24 to change velocity per hour into velocity per day.

Table VII.

Concentration of amide	0.015	0.03	0.04	0.06	0.12	0.20	0.30
Dilution	66.67	33.33	25.00	16.67	6.67	5.00	3.33
Benzamide	1.171	1.118	1.107	1.076	.....	.....	.....
Acetamide	.....	3.399	3.382	3.389	3.367	3.336	3.235

The same results are represented graphically below (Fig. I).

It appears that with benzamide, the velocity of the reaction decreases as the concentration of the amide increases, while for acetamide the velocity remains constant within the limits of experimental error till comparatively high concentrations are reached and then there is a decrease of the velocity with further increase of the concentration. The conduct of the benzamide is what was to have been expected according to the hypothesis of Acree and Nirdlinger.

In the work of Remsen and Reid,[1] done twelve years ago, on the hydrolysis of acid amides for the purpose of obtaining evidence bearing on the "hindrance" theory of Victor Meyer, a few amides were studied at concentrations of 0.04 and 0.02 normal relative to the amide. The results[2] in Table VIII

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[1] THIS JOURNAL, **21**, 284–348, and **24**, 397–424.

[2] *Ibid.*, **21**, 340, 341.

are taken from the work then published, each of the constants quoted being the average of a series.

Table VIII.—With Hydrochloric Acid at 100°.

Concentration of amide	0.02	0.04
p-Nitrobenzamide	0.0256	0.0236
p-Chlorbenzamide	0.0200	0.0179
m-Brombenzamide	0.0210	0.0184
p-Brombenzamide	0.0180	0.0145
With Barium Hydroxide at 100°.		
m-Brombenzamide	0.283	0.273

In the case of the *m*-brombenzamide the hydrolysis went on with barium hydroxide 3.7 per cent. faster in the 0.02 normal than in the 0.04 normal solution. In the present work it is found that benzamide is hydrolyzed by the same base 3.9 per cent. faster in a 0.03 normal than in a 0.06 normal solution. When acid was used as catalyst, a greater differ-

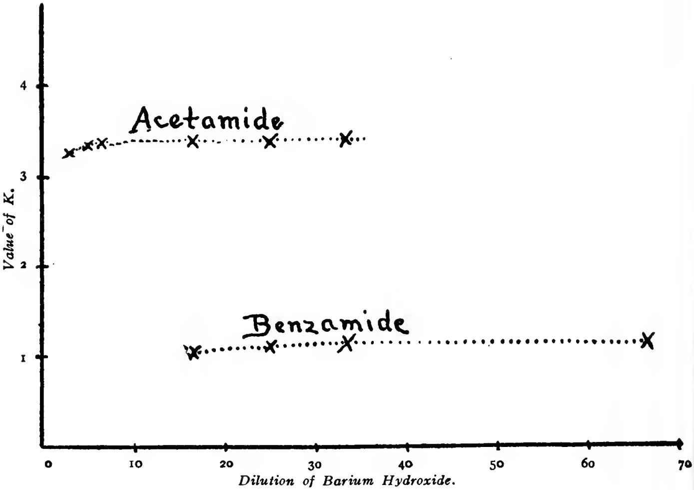

Fig. I.

ence, amounting to about 10 per cent., was found at the two concentrations of the amide. This agrees well with the greater differences found by Acree and Nirdlinger when hydrochloric acid was used as catalyst. In all cases the velocity of the reaction increases as the concentration of the amide diminishes, as is demanded by the theory, since the smaller the actual amount of amide present, which is a very weak base, the greater proportion of that small amount which will combine with the catalyst ion to form the reactive complex ion.

Effect of Neutral Salts.

Turning to columns 1 and 2 of Table VI, we find the average velocity, when the solution is 1 normal with respect to barium chloride, is 0.1400 as compared with an average of 0.1416 when no neutral salt is added. This difference, of about one per cent., though small compared with the experimental error, yet appears to be real since the difference is in the same direction in all eight of the experiments. Remsen and Reid[1] found that sodium sulphate diminished the rate of hydrolysis of the nitrobenzamides by caustic soda. Comparing the velocities found in column 3 of Table VII with those found in column 4 we find that the addition of one-half mole of barium acetate lowers the reaction velocity about six per cent. It is surprising that the acetate should be so much more effective than the chloride. The retarding influence of the barium acetate formed during the reaction accounts, in part, for the low values found for long-time periods.

Change of Velocity with Change of Concentration of Base.

The range of concentrations, from 0.35 to 0.05 normal, is not as great as is desirable, but was limited by the comparatively small solubility of the barium hydroxide. The average velocities from Tables II and VI are brought together in Table IX, those for acetamide being multiplied by 24 to make them comparable as to time periods with those for benzamide.

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[1] This Journal, **21**, 342.

Table IX.

Concentration of base	0.3489	0.30	0.20	0.10	0.05
Dilution of base	2.89	3.33	5.00	10.00	20.00
Benzamide	1.118	1.087	0.963	0.865	.....
Acetamide	3.40	3.42	3.35	3.36	3.38

These are shown graphically in the diagram (Fig. II). With benzamide, the velocity goes down steadily and regularly with increase of the dilution of the base. In the case of acetamide the change is much less and the uncertainty of the data is greater so that a conclusion is difficult, but the drift is in the same direction as with benzamide.

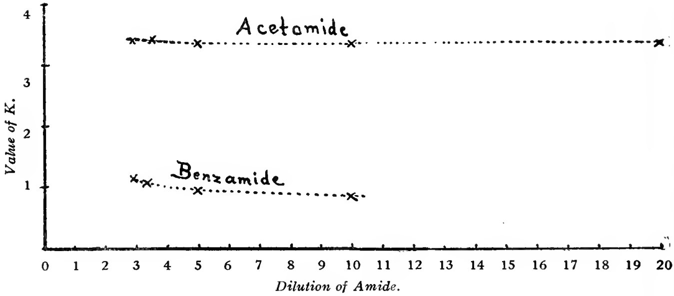


Fig. II.

The Temperature Coefficient of the Reaction.

In previous work,[1] I found the velocity for 0.04 normal benzamide with 0.1 normal barium hydroxide at 100° to be 0.0944. In this the time was measured in minutes so that this must be multiplied by 1440 to change it to days. This gives 136.2, which, divided by 0.865, the velocity now found for the same concentrations of amide and base at 25°, shows that the reaction proceeds 157.5 times as fast at 100° as at 25°. This gives a temperature coefficient of 1.963 for each 10°.

My chief interest has been in making the measurements

[1] This Journal, **24**, 419.

and in a study of the facts: the theoretical side of the problem will be discussed in later papers by Professor Acree and his collaborators when more data have been accumulated.

Johns Hopkins University,
Baltimore, Md.,
Dec. 16, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXVIII.—THE TRANSFORMATION OF ALLYLPHTHALIMIDE INTO PROPENYLPHTHALIMIDE.

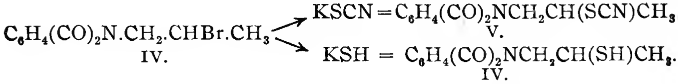
By Treat B. Johnson and D. Breese Jones.

Nomenclature.—New data are presented in this paper which contribute to our knowedge of the chemistry of propylene compounds, and in order to avoid confusion in distinguishing substitution products of this unsaturated hydrocarbon the terms *allyl* and *propenyl* are assigned to the groupings I and II, respectively. It seemed desirable to call attention to this

$$\begin{array}{ccc} -CH_2.CH:CH_2 & \quad -CH:CH.CH_3 & \quad CH_2:C.CH_3 \\ \text{I.} & \text{II.} & \text{III.} \end{array}$$

distinction of terms because of the many irregularities in the nomenclature of allyl and propenyl compounds which appear in the chemical literature. Attention has previously been called to this confusion of terms in a paper by August Klages.[1]

Seitz, in a paper entitled "Zur Kenntniss halogenhaltiger Amine der Fettreihe,"[2] showed that β-brompropylphthalimide, IV, reacts smoothly, in alcohol, with potassium thiocyanate and potassium sulphydrate, with direct replacement of the bromine atom, giving β-thiocyanpropylphthalimide, V, and β-mercaptopropylphthalimide, VI, respectively. He also examined the behavior of this bromide towards aniline and observed that they reacted at 150°, in a unique manner, with an interchange of the phenyl and bromisopropyl radicals,



$$\begin{array}{lcl} & \nearrow & KSCN = C_6H_4(CO)_2NCH_2CH(SCN)CH_3 \\ & & \qquad\qquad \text{V.} \\ \underset{\text{IV.}}{C_6H_4(CO)_2N.CH_2.CHBr.CH_3} & & \\ & \searrow & KSH = C_6H_4(CO)_2NCH_2CH(SH)CH_3. \\ & & \qquad\qquad \text{IV.} \end{array}$$

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[1] Ber. d. chem. Ges., **35**, 2247 (1902).

[2] *Ibid.*, **24**, 2627 (1891).

giving phenylphthalimide, VII, and β-brompropylamine, VIII. A part of the bromide, however, reacted normally, giving as a secondary product of the reaction β-anilinopropylphthalimide, IX. These changes are expressed by the following scheme:

$$\begin{tikzcd}[row sep=small]
C_6H_4(CO)_2N.CH_2CHBrCH_3 + & \\
& \underset{\text{VII.}}{C_6H_4(CO)_2N.C_6H_5} + \underset{\text{VIII.}}{NH_2.CH_2CH.BrCH_3} \\
C_6H_5NH_2 \arrow[ur] \arrow[dr] & \\
& \underset{\text{IX.}}{C_6H_4(CO)_2NCH_2CH(NHC_6H_5)CH_3.}
\end{tikzcd}$$

Bartholdy[1] later investigated the action of alkali on this bromide and observed that the bromine atom could be replaced by the hydroxyl group by digestion with an alcoholic solution of potash, giving β-hydroxypropylphthalimide, X:

$$C_6H_4(CO)_2NCH_2CHBrCH_3 + KOH = \\ KBr + \underset{\textbf{X.}}{C_6H_4(CO)_2NCH_2.CHOH.CH_3.}$$

He apparently obtained no evidence of the formation of an allyl or a propenyl derivative by removal of hydrobromic acid.

These observations suggested to the writer that β-brompropylphthalimide would react normally with the sodium salt of an acid methylene compound, —CO—CH$_2$—CO—. For example, theoretically it would be expected to combine with the sodium salt of diethyl malonate, giving the unknown diethyl β-methyl-γ-phthalimidoethylmalonate, XI:

$$C_6H_4(CO)_2NCH_2.CHBr.CH_3 + NaCH(COOC_2H_5)_2 = \\ \underset{\text{XI.}}{C_6H_4(CO)_2N.CH_2CH(CH_3)CH(COOC_2H_5)_2.}$$

The isomeric diethyl phthalimidopropylmalonate, XII, has been synthesized by Gabriel[2] by the action of the isomeric γ-brompropylphthalimide on diethyl sodiummalonate:

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[1] Ber. d. chem. Ges., **40**, 4400 (1907).

[2] *Ibid.*, **23**, 1768 (1890).

$$C_6H_4(CO)NCH_2CH_2CH_2Br + NaCH(COOC_2H_5)_2 = \\ C_6H_4(CO)_2NCH_2CH_2CH_2CH(COOC_2H_5)_2.$$

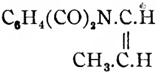
XII.

We now find that β-brompropylphthalimide does not react with diethyl sodiummalonate like its isomer, giving the ester, XI, but loses a molecule of hydrobromic acid under these conditions, giving a good yield of the hitherto unknown *propenylphthalimide*, XIII, with regeneration of diethyl malonate:

$$C_6H_4(CO)_2NCH_2CHBrCH_3 + NaCH(COOC_2H_5)_2 = \\ NaBr + CH_2(COOC_2H_5)_2 + C_6H_4(CO)_2N.CH:CHCH_3.$$

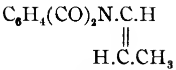
XIII.

We furthermore have obtained evidence which indicates that there are two isomeric modifications of propenylphthalimide. Two compounds having this empirical formula were isolated and had the same melting point, but they differed in color, crystalline form and solubility. Owing to the fact, however, that one of the isomers was not obtained in sufficient quantity for a careful examination it was impossible to establish definitely the nature of this isomerism. It seems very probable, nevertheless, that we are dealing here with a case of isomerism similar in character to that observed by Wislicenus[1] in the case of the stereoisomeric butylenes, XVI and XVII, and by Hoering and Baum[2] in the case of the isosafroles, XVIII and XIX.



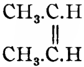
$$\begin{array}{r} C_6H_4(CO)_2N.C.H \\ \| \\ CH_3.C.H \end{array}$$

XIV.



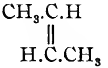
$$\begin{array}{l} C_6H_4(CO)_2N.C.H \\ \| \\ H.C.CH_3 \end{array}$$

XV.



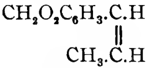
$$\begin{array}{r} CH_3.C.H \\ \| \\ CH_3.C.H \end{array}$$

XVI.



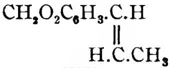
$$\begin{array}{l} CH_3.C.H \\ \| \\ H.C.CH_3 \end{array}$$

XVII.



$$\begin{array}{r} CH_2O_2C_6H_3.C.H \\ \| \\ CH_3.C.H \end{array}$$

XVIII.



$$\begin{array}{l} CH_2O_2C_6H_3.C.H \\ \| \\ H.C.CH_3 \end{array}$$

XIX.

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[1] Ann. Chem. (Liebig), **313**, 207 (1900).

[2] Ber. d. chem. Ges., **42**, 3076 (1909).

Several attempts were made to prepare propenylphthalimide by the action of other reagents than diethyl sodiummalonate on β-brompropylphthalimide. The halide, however, showed a remarkable inertness in many cases where a reaction would be expected to take place. No evidence of the formation of allyl- or propenylphthalimide was obtained when the bromide was warmed in alcohol with metallic zinc or silver benzoate or when digested with boiling pyridine. Sodium phenolate, on the other hand, reacted immediately with the bromide, on warming in alcoholic solution, giving the propenyl compound.

Propenylphthalimide is characterized by its yellow color, while the isomeric allyl compound is colorless. It is less soluble in alcohol than allylphthalimide and melts at 151°. It does not add hydrobromic acid to give the original β-brompropylphthalimide and does not rearrange to the isomeric allyl derivative when heated above its melting point. Allylphthalimide is not transformed into propenylphthalimide by treatment with alcoholic potash. This observation is of interest because it shows that allylphthalimide is not an intermediate product of the reaction when β-brompropylphthalimide undergoes conversion to the propenyl compound by the action of diethyl sodiummalonate. On the other hand it undergoes saponification under these conditions, giving smoothly the corresponding allylphthalamic acid, XX, melting at 112°. Allyl- and propenylphthalimides are converted into allylphthalamic acid, XX, and propenylphthalamic acid, XXI, (melting at 151°), respectively, when warmed with sodium ethylate:

$$\underset{\text{XX.}}{HOOCC_6H_4CONHCH_2CH:CH_2}, \quad \underset{\text{XXI.}}{HOOCC_6H_4CONHCH:CHCH_3}.$$

The regularity with which the removal of halogen acids takes place in certain halogen compounds, giving ethylene derivatives, led in early years to the formulation of rules governing the manner of removal which might be expected to take place. One of these is as follows: "*When the halogen atom is between two hydrogenated carbon atoms, the hydrogen is removed from that carbon having the least number of hydrogen* *atoms*."[1] It was of interest in connection with our work to make a classification of certain types of halides in order to determine the general application of this rule. A careful review of the literature now reveals the fact that the majority of halides of the general formula under examination,

$$X.CH_2.CH\,hal.CH_3,$$

lose the halogen acid in conformity with the above rule, as we have observed in the case of β-brompropylphthalimide. There are, however, several exceptions which are of interest.

It is therefore interesting to note in this connection that, of 27 different halides of the above type which we have reviewed, 17 have undergone transformations by the action of alkali and other reagents, giving propenyl compounds. The most striking feature of this list of 17 halides (Table I) is the variety of organic radicals which have been substituted for X. An examination of the tables will show conclusively that an unsaturated condition, or the positive and negative character of the groups X, are not the deciding factors in governing the position the double bond will take.

The radicals substituted for X (Table II) which have favored the formation of allyl compounds among this series of 27 halides are represented only by β-naphthylsulfone, $C_{10}H_7SO_2$, hippuryl, $C_6H_5CONHCH_2CO$, and a series of aminoalkyl groups,[2] in which the amino radical occupies positions 4 or 5 with respect to the halogen atom. It is especially noteworthy that α-naphthylsulfone-β-brompropane,[3] XXII, should give an allyl derivative, XXIII, since it represents a type of compounds which theoretically would be expected to give propenyl derivatives, XXIV.

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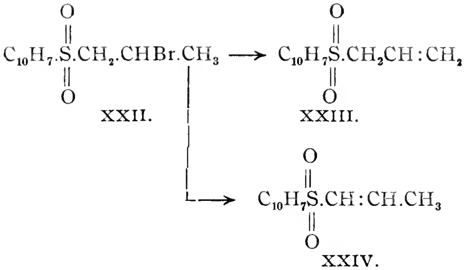
[1] Beilstein's Handbuch, I, 95; and Alexeyeff and Mathews: General Principles of Organic Synthesis, pp. 108.

[2] Merling: Ann. Chem. (Liebig), **264**, 310 (1891). Jacobi and Merling: *Ibid.*, **278**, 1 (1893).

[3] Troeger and Artmann: J. prakt. Chem., **53**, 492 (1896).



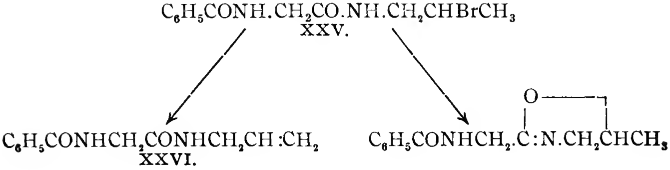
$$C_{10}H_7.\overset{O}{\underset{O}{S}}.CH_2.CHBr.CH_3 \longrightarrow C_{10}H_7\overset{O}{\underset{O}{S}}.CH_2CH:CH_2$$

XXII. XXIII.

$$\longrightarrow C_{10}H_7\overset{O}{\underset{O}{S}}.CH:CH.CH_3$$

XXIV.

That β-brompropylhippurylamide,[1] XXV, should react with sodium ethylate and diethyl sodiummalonate, giving an allyl derivative, XXVI, while β-brompropylphthalimide, under the same conditions, gives a propenyl compound, is truly remarkable. Apparently it is the only acylamide of this type which has been observed to break down in this manner, giving an ethylene compound. Compounds of this type usually decompose, in the presence of alkali, in a characteristic way, giving oxazolines:[2]



$C_6H_5CONH.CH_2CO.NH.CH_2CHBrCH_3$

XXV.

$C_6H_5CONHCH_2CONHCH_2CH:CH_2$

XXVI.

$C_6H_5CONHCH_2.C:N.CH_2CHCH_3$

Table I.

Organic radicals which favor the formation of propenyl compounds: $X.CH_2.CHhal.CH_3 \longrightarrow X.CH:CH.CH_3$.

X = CH_3,[3] C_2H_5,[4] C_3H_7,[5] C_4H_9,[6] $CH_2:CH.CH_2$,[7] CH_3CO,[8]

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[1] Diels and Beccard: Ber. d. chem. Ges., **39,** 4126 (1906).

[2] Gabriel: *Ibid.*, **22,** 2984. Gabriel and Heymann: *Ibid.*, **23,** 2493. Gabriel and Lauer: *Ibid.*, **23,** 91. Prager: *Ibid.*, **22,** 2991. Hirsch: *Ibid.*, **23,** 964. Elfeldt: *Ibid.*, **24,** 3218.

[3] Luynes: Ann. Chem. (Liebig), **128,** 331.

[4] Wurtz: *Ibid.*, **123,** 203; **127,** 55; **148,** 131. Wagner and Saytzew: *Ibid.*, **175,** 373; **179,** 302.

[5] Erlenmeyer and Wanklyn: *Ibid.*, **135,** 134. Hecht and Munier: Ber. d. chem. Ges., **11,** 1154.

[6] Schorlemmer: Ann. Chem. (Liebig), **166,** 177.

[7] Grinner: Beilstein's Handbuch, I, 133.

[8] Blaise: Bull. soc. chim., [3] **33,** 45.

NH_2,[1] $C_2H_5O(NH)C$,[2] NH_2CO,[2] $C_6H_5CH_2NH$(?),[3] COOH,[4] C_6H_5,[5] $C_6H_4.CH_3$,[5] Br,[6] $BrCH_2.CH_2$,[6] $CH_3CHBr.CH_2$,[7] CH_3CHCH_3.[7]

Table II.

Organic radicals which favor the formation of allyl compounds: $X.CH_2.CHhal.CH_3 \longrightarrow X.CH_2.CH : CH_2$.

X = NH_2CH_2,[8] $NH_2(CH_3)CHCH_2$, $NH_2(CH_3)CHCH(CH_3)$, $NH_2(CH_3)CHCH(CH_2CH : CH_2)$, $N(CH_3)_2CH_2CH_2$, $N(CH_3)_2(CH_2)_2CH_2$, $N(CH_3)_2(CH_3)CHCH_2$, $N(CH_3)_2CH_2CH(CH_3)$,[9] $C_6H_5CONHCH_2CONH$,[10] $C_{10}H_7SO_2$[11]

EXPERIMENTAL PART.

Allylphthalimide, $C_6H_4(CO)_2N.CH_2CH : CH_2$.—This compound was prepared according to Kay's[12] method by heating allyl isothiocyanate with phthalic anhydride:

$$C_6H_4(CO)_2O + CH_2 : CHCH_2NCS = C_6H_4(CO)_2NCH_2.CH : CH_2 + COS.$$

Thirty grams of freshly distilled allyl isothiocyanate were mixed with 46.8 grams (1 mol.) of finely powdered phthalic anhydride and heated in an oil bath at 135°–140°. The anhydride soon went into solution, giving a yellow liquid. After heating for about 70 hours, when the evolution of carbon oxysulphide had practically ceased, the liquid was then cooled and washed several times with hot water, to remove phthalic acid. The allylphthalimide then solidified and was purified by distillation under diminished pressure and recrystallization from carbon bisulphide. It crystallized in large colorless prisms which melted at 71° to an oil. Allylphthalimide is

[1] Hirsch: Ber. d. chem. Ges., **23,** 968.
[2] Pinner: *Ibid.*, **17,** 2008.
[3] Uedinck: *Ibid.*, **32,** 972.
[4] Balbiano: *Ibid.*, **11,** 348. Pinner: *Ibid.*, **12,** 2058.
[5] Errara: Gazz. chim. ital., **14,** 318: **14,** 283.
[6] Solinina: J. russ. physik. chem. Ges., **30,** 862. Centralb., **1899,** I, 248.
[7] Schramm: Ber. d. chem. Ges., **30,** 637.
[8] Leuchmann: Ber. d. chem. Ges., **29,** 1431.
[9] Jacobi and Merling: *Loc. cit.*
[10] Diels and Baccard: *Loc. cit.*
[11] Troeger and Artmann: *Loc. cit.*
[12] Ber. d. chem. Ges., **26,** 2850 (1893).

very soluble in ether, carbon bisulphide, benzene, petroleum ether and alcohol, and insoluble in water. It can be crystallized from alcohol. The total yields and relative proportions of allylphthalimide obtained in four experiments by the above method are given in the following table:

	Phthalic anhydride. Grams.	Allyl isothiocyanate. Grams.	Yield of allylphthalimide. Grams.	Yield. Per cent.
1	56.0	33.7	41.0	58.5
2	36.5	22.5	30.5	66.1
3	40.5	25.0	34.5	67.4
4	48.6	30.0	48.0	78.1

β-Brompropylphthalimide,[1] $C_6H_4(CO)_2N.CH_2.CHBr.CH_3$.—When allylphthalimide is suspended in a strong hydrobromic acid solution, addition of hydrobromic acid to the double bond takes place immediately. We found, however, that our yields of the above bromide were greatly improved by using an acid which had been saturated with hydrobromic acid gas at —5° to 0°. The best yields were obtained under the following conditions: Thirty grams of pulverized allylphthalimide were suspended, in a strong, glass-stoppered bottle, in 150 cc. of hydrobromic acid saturated with hydrobromic acid gas at —5°. Practically all of the phthalimide dissolved in a few minutes, giving a clear solution. After standing at room temperature for two or three days, with occasional shaking, a dense mass of crystals separated, which were filtered on asbestos by suction, washed with cold water and allowed to dry in the air. The crude product usually melted sharply at 105° to a clear oil. It melted, after purification by recrystallization from alcohol, at 110°.

β-Brompropylphthalimide crystallizes from 95 per cent. ethyl alcohol in colorless, fibrous, glistening needles. It is easily soluble in ethyl and methyl alcohols, carbon bisulphide, ether, chloroform and benzene and slightly soluble in petroleum ether and boiling water. The yields and relative proportions of β-brompropylphthalimide obtained in three preparations are given in the following table:

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[1] Seitz: *Loc. cit.*

	HBr. cc.	Allylphthalimide. Grams.	Yield of bromopropylphthalimide. Grams.	Yield. Per cent.
1	200	47.0	55.0	81.6
2	150	30.0	30.0	70.0
3	124	31.0	35.0	78.8

Action of Diethyl Sodiummalonate on β-Brompropylphthalimide.

Formation of Propenylphthalimide, $C_6H_4(CO)_2N.CH:CH.CH_3$.—Thirty-one and three-tenths grams of diethyl malonate were added to a cold solution of sodium ethylate, prepared by dissolving 4.5 grams of sodium in 250 cc. of absolute alcohol. Fifty-two and three-tenths grams of β-brompropylphthalimide were then dissolved in the solution and the mixture digested on the steam bath for two hours, when the solution reacted neutral to litmus and turmeric. After filtering off the undissolved sodium bromide, the solution was concentrated under diminished pressure and the residue obtained then extracted with a small volume of ether. A crystalline substance, insoluble in ether, was obtained here, which was separated by filtration, washed with cold water and purified by crystallization from alcohol (see below for the examination of the ether filtrate). The compound separated on cooling in characteristic, light-yellow blocks, which melted at 151° to an oil. The analytical determinations gave the following results:

I. Nitrogen determinations by Kjeldahl method.

II. 0.1280 gram substance gave 0.3327 gram CO_2 and 0.0603 gram H_2O.

	Calculated for $C_{11}H_9O_2N$.	Found. I.	Found. II.
C	70.58	70.89	....
H	4.81	5.27	....
N	7.48	7.38	7.16

Molecular weight determination in benzene solution:

0.6670 gram of substance dissolved in 14.11 grams benzene caused a depression of 1°.283 in the freezing point of the solvent.

	Calculated for $C_{11}H_9O_2N$.	Found.
Mol. weight	187	180.6

A solution of propenylphthalimide decolorized bromine water at once. It is readily soluble in benzene, chloroform and carbon bisulphide; moderately soluble in alcohol and insoluble in petroleum ether and water. The yellow color of the crystals is apparently characteristic and not due to impurities. The yield of purified material was 8 grams.

Examination of the Above Ether Filtrate.—When this was allowed to evaporate in air we obtained a colorless oil, from which about 5 grams of the propenyl derivative, mixed with a little β-propylphthalimide, deposited on standing. The oil was dissolved in petroleum ether, dried over sodium sulphate and then purified by distillation. We obtained 19 grams of unaltered diethyl malonate boiling at 194°-202°, which represented about 60 per cent. of the original ester used. The dark-colored oily residue which remained in the distilling bulb had the properties of an acid and dissolved in cold alkali with the exception of a small amount of crystalline material. This was separated, dissolved in hot alcohol, and some benzene added to the solution, when about 0.5–0.7 gram of large, colorless, glistening, micalike plates separated. This substance did not contain bromine and melted at 150°–151°, to an oil. A mixture of this compound and the propenyl compound melted at the same temperature. It was very soluble in alcohol and moderately soluble in benzene. Nitrogen and molecular weight determinations proved that it was isomeric with propenylphthalimide. Owing to the fact, however, that the yield of this interesting substance was so small, it was impossible to make a thorough study of its properties. Whether it is a stereoisomeric modification or a physical isomer we are unable to say at the present time. Nitrogen determinations by Kjeldahl method:

	Calculated for $C_{11}H_9O_2N$.	Found.	
		I.	II.
N	7.48	7.18	7.3

Molecular weight determination in benzene solution:

0.3254 gram of substance dissolved in 12.27 grams of benzene caused a depression of 0°.719 in the freezing point of the solvent.

	Calculated for $C_{11}H_9O_2N$.	Found.
Mol. weight	187	180.7

Action of Sodium Phenolate on β-Brompropylphthalimide.

Formation of Propenylphthalimide.—Two grams of the bromide and 0.7 gram of phenol, in the form of sodium phenolate, were dissolved in absolute alcohol and digested on the steam bath for 6–7 hours. The solution was then cooled and the undissolved sodium bromide filtered off. On concentrating the alcohol filtrate a viscous liquid was obtained which we triturated with water to remove any sodium bromide held in solution. On standing, this oil partially solidified and deposited a yellow crystalline substance which crystallized from 95 per cent. alcohol. More of the substance continually separated on standing. The compound separated from alcohol, on cooling, in stout, yellow blocks which melted at 150°–151° to a clear oil, without effervescence. It was identified as propenylphthalimide. A mixture of this substance and a sample of propenylphthalimide described in the preceding experiment melted at exactly the same temperature.

Nitrogen determination (Kjeldahl):

	Calculated for $C_9H_{11}O_2N$.	Found.
N	7.48	7.4

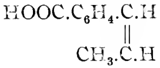
Action of Sodium Ethylate on Propenylphthalimide.

Formation of Propenylphthalamic Acid, $HOOC.C_6H_4.CONHCH:CH.CH_3$.—Two grams of propenylphthalimide were added to a solution of sodium ethylate prepared by dissolving 0.72 gram of sodium (1 molecule) in 25 cc. of absolute alcohol. After 2 hours' digestion the alcohol was then evaporated when a syrupy residue was obtained. This was dissolved in cold water and the solution acidified with hydrochloric acid, when a red oil separated which dissolved immediately in ether. When the ether was allowed to evaporate 1.6 grams of the phthalamic acid separated as a crystalline powder. It is extremely soluble in water and alcohol and difficultly soluble in ether; insoluble in petroleum ether, benzene and chloroform. When it is dissolved in absolute alcohol and the solution allowed to evaporate at ordinary temperature the acid separates as a thick, viscous syrup which finally crystallizes after long standing. It melts at 152° to a clear oil.

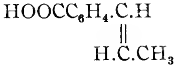
Nitrogen determination (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N$.	Found. I.	II.
N	6.83	6.73	6.7

Propenylphthalamic acid is precipitated from an alkaline solution by addition of hydrochloric acid as a viscous substance, which assumes, slowly, a crystalline condition only after long standing. This is the most characteristic property of this acid. The fact that the allylphthalamic acid shows no tendency to undergo such changes under the same conditions suggests that we have here two stereoisomeric modifications of propenylphthalamic acid, one form a syrup at ordinary temperature and the other a solid melting at 152°. Whether the solid melting at 152° represents the *cis* or *trans* modification we have no evidence.



$$\begin{array}{r} HOOC.C_6H_4.C.H \\ \| \\ CH_3.C.H \end{array}$$



$$\begin{array}{l} HOOCC_6H_4.C.H \\ \quad\quad\quad\quad \| \\ \quad\quad\quad\quad H.C.CH_3 \end{array}$$

This syrupy, labile propenylphthalamic acid is undoubtedly one of the products of the reaction when diethyl sodiummalonate acts on β-brompropylphthalimide. A viscous oil having acid properties is always obtained in this reaction and the quantity formed varies according to the conditions employed. Its formation explains the fact that unaltered β-brompropylphthalimide is always present even after the tests with turmeric and litmus indicate a neutral reaction.

Action of Sodium Ethylate on β-Brompropylphthalimide.—Three grams of β-brompropylphthalimide and 0.26 gram of sodium were dissolved in 15 cc. of absolute alcohol and the solution digested until neutral to turmeric (1.5 hours). On cooling, a mixture of sodium bromide and unaltered β-brompropylphthalimide separated. They were separated by filtration and washed with water to remove sodium bromide, when we recovered 1.0 gram of the β-brompropylphthalimide melting at 110°. The alcoholic filtrate was concentrated to a syrup, which was dissolved in cold water and filtered. The addition of hydrochloric acid precipitated a heavy, viscous oil, which possessed all the properties of labile propenylphthalamic acid. It did not contain bromine. We obtained no evidence of the formation of any allyl- or propenylphthalimide.

β-Brompropylphthalimide was recovered unaltered after digestion in benzene with zinc dust for 6 hours, and also after digestion in alcohol for 14 hours with silver benzoate. One gram was dissolved in 4 cc. of pyridine and the solution boiled for 5 hours. Water was then added to the cooled solution when the unaltered bromide separated and melted at 108°–110° without further purification.

Action of Sodium Ethylate on Allylphthalimide.

Formation of Allylphthalamic Acid, $HOOC.C_6H_4.CO.NH.CH_2.CH:CH_2$.—Five grams of allylphthalimide and 1.2 grams of sodium were dissolved in 50 cc. of absolute alcohol and the solution heated on a boiling water bath for 2 hours. On cooling, the sodium salt of allylphthalamic acid separated. The excess of alcohol was removed by evaporation, the salt dissolved in water and the solution acidified with hydrochloric acid. The allylphthalamic acid separated at once in crystalline form and melted at 112° to oil. This melting point was not changed by further attempts at purification. The acid is insoluble in cold ether, but extremely soluble in warm water, alcohol and benzene. It crystallizes best from a mixture of alcohol and ether.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N$.	Found.
N	6.83	6.68

This same acid is also obtained in the form of its potassium salt by gentle warming of allylphthalimide with the calculated amount of potassium hydroxide in alcohol. If digested with alkali for a prolonged period on the water bath, it undergoes complete decomposition, giving allylamine and *o*-phthalic acid melting at 199°. We obtained no evidence of any formation of propenylphthalimide or propenylphthalamic acid.

New Haven, Conn.,
Dec. 24, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXIX.—RESEARCHES ON PYRIMIDINES: ON THE CONDENSATION OF THIOUREA WITH ESTERS OF ALLYLMALONIC ACID AND SOME ALKYL-SUBSTITUTED ALLYLMALONIC ACIDS.

By Treat B. Johnson and Arthur J. Hill.

[FIFTIETH PAPER.]

In this paper we describe a number of new condensation products which we have obtained by condensing thiourea with diethyl allylmalonate,[1] I, diethyl allylbenzylmalonate, II, and diethyl diallylmalonate,[2] III.

$$CH_2{:}CHCH_2CH(COOC_2H_5)_2$$
I.

$$CH_2{:}CHCH_2(C_6H_5CH_2)C(COOC_2H_5)_2$$
II.

$$(CH_2{:}CHCH_2)_2C(COOC_2H_5)_2$$
III.

It is a well-known fact that unsaturated acids—olefincarboxylic acids—which contain a double bond between the γ,δ positions, easily undergo isomerization to γ-lactones. This change can be effected in different ways, as by distillation of the unsaturated acid, by addition of a halogen acid and its subsequent removal with closing of the ring, or by warming of the acid with dilute sulphuric acid. The simplest unsaturated monobasic and dibasic acids of this type, viz., allylacetic, IV, allylmalonic, V, and diallymalonic, VI, for example, are all transformed smoothly, under proper conditions,

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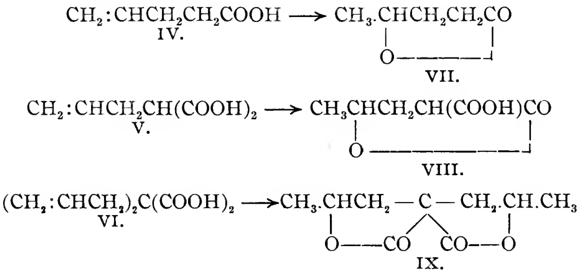
[1] Conrad and Bischoff: Ann. Chem. (Liebig), **204**, 168.

[2] Conrad and Bischoff: *Loc. cit.*

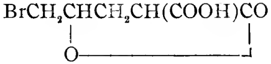
into γ-methylbutyrolactone,[1] VII, γ-methylbutyrolactone-α-carboxylic acid.,[2] VIII, and γ,γ-dimethyldibutyrolactone,[3] IX, respectively.



$$\underset{\text{IV.}}{CH_2{:}CHCH_2CH_2COOH} \longrightarrow \underset{\text{VII.}}{CH_3.CHCH_2CH_2CO}$$

$$\underset{\text{V.}}{CH_2{:}CHCH_2CH(COOH)_2} \longrightarrow \underset{\text{VIII.}}{CH_3CHCH_2CH(COOH)CO}$$

$$\underset{\text{VI.}}{(CH_2{:}CHCH_2)_2C(COOH)_2} \longrightarrow \underset{\text{IX.}}{CH_3.CHCH_2-C-CH_2.CH.CH_3}$$



$$BrCH_2CHCH_2CH(COOH)CO$$

X.

Fittig and Hjelt,[4] who investigated very thoroughly the action of hydrobromic acid and bromine on allyl fatty acids, were unable to obtain, in a pure state, γ-brompropylmalonic, XI, or γ,δ-dibrompropylmalonic, XII, acids by addition

$$\underset{\text{XI.}}{CH_3CHBrCH_2CH(COOH)_2}, \qquad \underset{\text{XII.}}{BrCH_2.CHBr.CH_2CH(COOH)_2}$$

of hydrobromic acid and bromine, respectively, to allylmalonic acid. They both underwent decomposition, even at ordinary temperature, giving the corresponding γ-methylbutyrolactone-α-carboxylic acid, VIII, and γ-brommethylbutyrolactone-α-carboxylic acid, X. Furthermore, they observed also that the formation of γ-lactones was not prevented by using the esters instead of the acids. The same lactone, for example, was obtained by the action of bromine on diethyl diallylmalonate as was obtained by the addition of bromine to the corresponding acid.

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[1] Messerschmidt: Ann. Chem. (Liebig), **208**, 97.

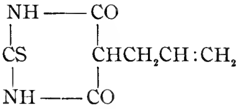
[2] Hjelt: *Ibid.*, **216**, 53.

[3] Hjelt: *Loc. cit.*

[4] Ann. Chem. (Liebig), **216**, 52. Hjelt: Ber. d. chem. Ges., **15**, 627.

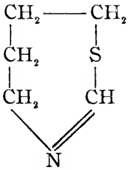
Owing to this instability of the γ- and γ,δ-halogen substituted propylmalonic acids, they are of limited value for synthetical purposes. A derivative, therefore, of allylmalonic acid, in which the carboxyl groups are linked in a manner so as to prevent lactone formations after addition of halogen acids and halogens to the ethylene linking, would be of especial interest. With the object in view of preparing a compound of this type, we therefore examined the behavior of diethyl allylmalonate towards thiourea. Theoretically they would be expected to react normally, giving the unknown allylthiobarbituric acid, XIII:

$CH_2{:}CHCH_2CH(COOC_2H_5)_2 + CS(NH_2)_2 =$

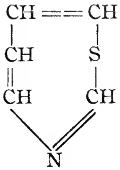


XIII.

We now find that diethyl allylmalonate condenses in a unique manner with thiourea, giving a stable, cyclic derivative—μ-amino-α-keto-β-carbethoxy-δ-methyltetrahydrohexathiazole, XVIII. This is a representative of a new class of cyclic compounds, tetrahydrohexathiazoles, XIV, of which the mother substance would be the *hexathiazole*[1] XV. Derivatives of analogous, six-membered rings containing sulphur and oxygen, viz., *penthiazolines*, XVI, and *pentoxazolines*, XVII, have been synthesized by Gabriel and his coworkers.[2]



XIV.



XV.

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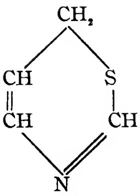
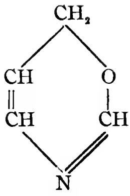
[1] Nomenclature: Traumann: Ann. Chem. (Liebig), **249**, 34. Krekeler: Ber. d. chem. Ges., **19**, 3266.

[2] Gabriel and Lauer: Ber. d. chem. Ges., **23**, 95. Gabriel and Elfeldt: *Ibid.*, **24**, 3213. Elfeldt: *Ibid.*, **24**, 3218.

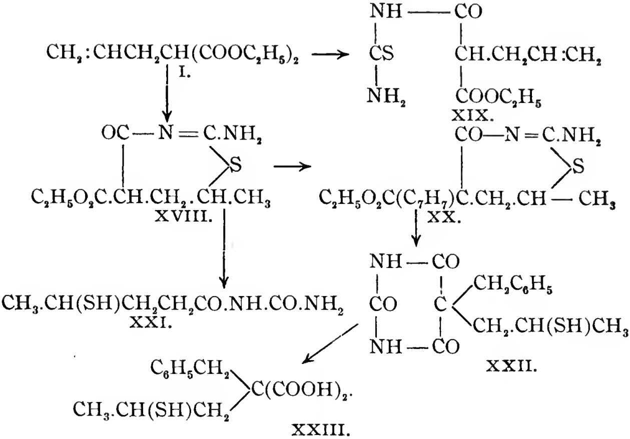


XVI.

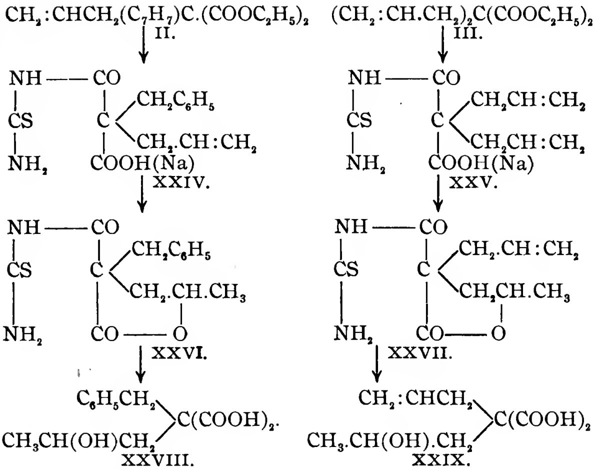


XVII.

That diethyl allylmalonate condensed, giving a *tetrahydrohexathiazole* derivative, XVIII, and not the isomeric thiourea compound, XIX, was established by the following facts: The hexathiazole, XVIII, was not desulphurized by the action of mercury oxide or lead acetate, indicating a linking of the sulphur atom between two carbon atoms. It behaved as a pseudo-thiourea and underwent hydrolysis, in acid solution, giving γ-mercapto-*n*-valerylurea, XXI. The compound reacted with benzyl chloride, in presence of sodium ethylate, giving a benzyl derivative, substituted on the carbon, XX. This alkyl derivative was converted quantitatively into 5,5-benzyl-β-mercaptopropylbarbituric acid, XXII, by hydrolysis with concentrated hydrochloric acid. Saponification of this pyrimidine with strong potash then gave smoothly the hitherto unknown β-mercaptopropylbenzylmalonic acid, XXIII. These reactions prove that thiourea reacts in its pseudo form with diethyl allylmalonate, and that the mercapto group –SH adds at the double bond of the allyl group, giving the cyclic derivative, XVIII. These various transformations are represented by the following formulas:



In order to determine whether alkyl derivatives of diethyl allylmalonate would condense with thiourea, in a similar manner as allylmalonic ester, giving the corresponding tetrahydrohexathiazoles, we also examined the behavior of diethyl allylbenzylmalonate, II, and diethyl diallylmalonate, III, towards this reagent. We now find that these two esters react with thiourea in an entirely different manner than diethyl allylmalonate. They condense practically quantitatively, in the presence of sodium ethylate, giving apparently the sodium salts of the corresponding acylthioureas, XXIV and XXV. When these salts were dissolved in water and the solutions acidified with hydrochloric or sulphuric acids, the acids immediately underwent isomerization to the corresponding γ-lactones, XXVI and XXVII. Their low melting points indicated a lactone structure, and they were desulphurized by the action of mercury oxide. Their constitution was established by the facts that they underwent a normal lactone hydrolysis, with potassium hydroxide, giving the corresponding β-hydroxypropylbenzylmalonic, XXVIII, and β-hydroxypropylallylmalonic, XXIX, acids, respectively, with formation of ammonia and hydrogen sulphide. These various changes are represented in the following manner:

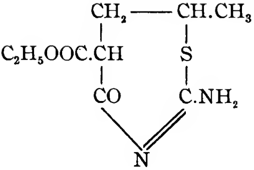


The observation that the two acids XXIV and XXV undergo isomerization, giving apparently γ-lactones, instead of condensing in a normal manner to give barbituric acid derivatives, is especially interesting. It is also a remarkable fact that thiourea reacts with diethyl allylmalonate with addition of –SH at the double bond of the allyl group, while the corresponding diallyl compound shows no tendency, under the same conditions, to give a tetrahydrohexathiazole, but condenses to a γ-lactone.

The study of the action of esters of unsaturated acids on thioureas, ureas, pseudothioureas and guanidines is being continued in this laboratory.

EXPERIMENTAL PART.

μ-Amino-α-keto-β-carbethoxy-δ-methyltetrahydrohexathiazole.—



.—Three and six-tenths grams of

sodium were dissolved in 40 cc. of absolute alcohol and 4.5 grams of thiourea added to the solution. Fifteen grams of diethyl allylmalonate (1 molecule) were then added and the solution heated in a boiling water bath. There was an immediate reaction and within a few minutes a magma of a colorless sodium salt was obtained. The mixture was then heated for 5 to 7 hours in order to complete the reaction and the excess of alcohol finally expelled by evaporation at 100°. The salt was then dissolved in the least possible quantity of cold water and an excess of dilute sulphuric acid added, and the solution cooled to 0°. The hexathiazole separated as a pink, crystalline precipitate. The compound was extremely soluble in alcohol and was purified by crystallization from hot water in which it is quite soluble. The aqueous solution must not, however, be heated to boiling as the compound slowly undergoes hydrolysis under these conditions, giving an oily, ill-smelling compound. On cooling it separates in pink-colored prisms, which melt at 88°–89° to a clear oil. The yield was 12.7 grams. The hexathiazole is not desulphurized by warming in aqueous and alcoholic solutions with mercury oxide, or with lead acetate in an alkaline solution. It dissolves in dilute sodium hydroxide solution, giving a characteristic purple-red solution which changes, on heating, to the color of a dilute Congo-red solution. It is not decomposed by boiling in alkaline solution and is precipitated unaltered on making the solution acid. The stability of the compound towards alkali was remarkable.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_9H_{14}O_3N_2S$.	Found. I.	II.	III.
N	12.17	12.24	12.24	12.2

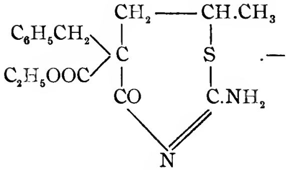
Hydrolysis with Hydrochloric Acid.

*Formation of γ-Mercapto-*n*-valerylurea,* $CH_3.CH(SH).CH_2CH_2.CO.NH.CO.NH_2$.—This compound was obtained by dissolving 1.8 grams of the above hexathiazole in 50 cc. of cold concentrated hydrochloric acid and then evaporating the solution to dryness on the steam bath. It is insoluble in cold water but soluble in warm absolute alcohol. It was purified for analysis by recrystallization from glacial acetic acid and melted at 186° with decomposition.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_6H_{12}O_2N_2S$.	Found. I.	Found. II.
N	16.00	16.2	16.2

μ-Amino-α-keto-β-carbethoxy-δ-methyl-β-benzyltetrahydrohexathiazole,

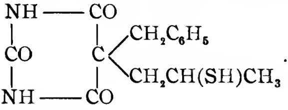


.—Sixty-two hundredths gram of sodium was dissolved in absolute alcohol and 6.2 grams of α-keto-β-carbethoxy-δ-methyl -μ- aminotetrahydrohexathiazole added to the solution, when the corresponding sodium salt separated at once. A molecular proportion of benzyl chloride (3.4 grams) was then added and the mixture heated until neutral to turmeric. The reaction was complete within a few minutes and after evaporating the excess of alcohol the benzylhexathiazole was purified by crystallization from 50 per cent. alcohol. It separated, on cooling, in colorless prisms melting at 221° to an oil without effervescence. The compound is soluble in boiling alcohol but insoluble in water. The yield of purified material was 4.0 grams.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{16}H_{20}O_3N_2S$.	Found. I.	Found. II.
N	8.75	8.76	8.73

5-β-Mercaptopropyl-5-benzylbarbituric Acid,

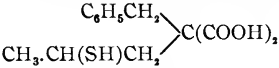


.—A quantitative yield of this pyrimidine was obtained by dissolving 4 grams of the above benzylhexathiazole in 50 cc. of cold, concentrated hydrochloric acid and then evaporating the solution to dryness on the steam bath. It is insoluble in cold water and alcohol, but crystallizes from glacial acetic acid in colorless prisms melting at 236° to an oil. The pyrimidine is not decomposed by short digestion with 50 per cent. potash solution, and separated unaltered on the addition of hydrochloric acid. It gave a strong test for sulphur.

Nitrogen determination (Kjeldahl):

	Calculated for $C_{14}H_{16}O_3N_2S$.	Found. I.	II.
N	9.59	9.5	9.7

β-Mercaptopropylbenzylmalonic Acid,



$$\begin{matrix} C_6H_5CH_2 \\ CH_3.CH(SH)CH_2 \end{matrix}\!\!>\!C(COOH)_2.$$

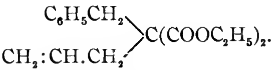
—This acid was obtained in the form of its monopotassium salt as follows: 2 grams of the above pyrimidine were dissolved in 6 cc. of a 50 per cent. potassium hydroxide solution and heated in a sealed tube at 130° for two hours. A clear solution was obtained having a strong odor of ammonia. Hydrochloric acid was then added in excess, when a characteristic, crystalline monopotassium salt of the malonic acid separated from the acid solution. There was no evidence of any evolution of hydrogen sulphide. The substance left a heavy inorganic residue when burned on a platinum foil and gave a positive test for sulphur.

Sulphur determination (Carius):

I. 0.1157 gram of substance gave 0.0891 gram of $BaSO_4$.

	Calculated for $C_{13}H_{15}O_4SK$.	Found.
S	10.45	10.58

Diethyl Allylbenzylmalonate,



$$\begin{matrix} C_6H_5CH_2 \\ CH_2{:}CH.CH_2 \end{matrix}\!\!>\!C(COOC_2H_5)_2.$$

—This ester was prepared by the action of allyl iodide on the sodium salt of diethyl benzylmalonate[1] in alcoholic solution, and also by the action of benzyl chloride on diethyl sodiumallylmalonate[1]. It is a colorless viscous oil which boils at 228°–230° under 60–65 mm. pressure.

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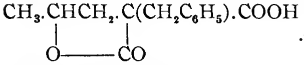
[1] Conrad and Bishoff: *Loc. cit.*

γ-Methyl-α-benzylbutyrolactone-α-carboxylic Acid,



$$\begin{array}{l}\mathrm{CH_3.CHCH_2.C(CH_2C_6H_5).COOH}\\ \quad\;| \qquad\quad\;\; | \\ \quad\mathrm{O}\text{———}\mathrm{CO}\end{array}$$

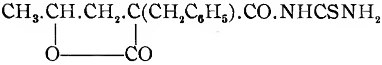
.—This was obtained as a syrup by saponification of diethyl allylbenzylmalonate: 1.7 grams of the ester were dissolved in 50 per cent. alcohol containing three molecular proportions of potassium hydroxide, and the solution boiled for one hour. After acidifying strongly with hydrochloric acid the solution was extracted repeatedly with ether and the latter then evaporated. A thick syrup was obtained which did not crystallize after standing for several hours. This was dissolved in cold, dilute ammonia, and the silver salt precipitated by adding an excess of silver nitrate solution. It separated as a colorless, granular precipitate, which was dried for analysis in a desiccator over concentrated sulphuric acid.

Silver determination:

I. 0.1894 gram substance gave 0.0722 gram Ag.

	Calculated for $C_{13}H_{12}O_4Ag$.	Found.
N	31.7	32.8

γ-Methyl-α-benzylbutyrolactone-α-carbonylthiourea,



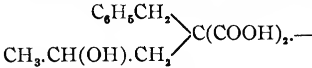
$$\begin{array}{l}\mathrm{CH_3.CH.CH_2.C(CH_2C_6H_5).CO.NHCSNH_2}\\ \quad\;| \qquad\qquad | \\ \quad\mathrm{O}\text{————}\mathrm{CO}\end{array}$$

.—One gram of sodium (2 molecules) was dissolved in 20 cc. of absolute alcohol and a molecular proportion of thiourea (1.6 grams) dissolved in the solution; 6.1 grams of diethyl allylbenzylmalonate were then added and the solution heated at 100° for five hours. We obtained a turbid solution which was heated in an open vessel to expel the excess of alcohol, and the sodium salt dissolved in water. On acidifying with hydrochloric acid a heavy, yellow, semisolid product separated which assumed a crystalline form on trituration with a little benzene. The lactonethiourea is soluble in warm alcohol and moderately soluble in benzene. It crystallizes from the latter in light yellow crystals which melt at 145°–146° to a clear oil without effervescence. It dissolves in cold concentrated hydrochloric acid and the solution can be evaporated to dryness without decomposition of the lactone.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_{14}H_{16}O_3N_2S$.	Found.	
		I.	II.
N	9.56	9.55	9.62

β-Hydroxypropylbenzylmalonic Acid,



$$\left.\begin{matrix} C_6H_5CH_2 \\ CH_3.CH(OH).CH_2 \end{matrix}\right> C(COOH)_2$$

.—Two grams of the preceding γ-lactone were dissolved in 6 cc. of a 50 per cent. potassium hydroxide solution and heated for two hours at 130°–150°. Ammonia was given off and when the solution was acidified with hydrochloric acid hydrogen sulphide gas was evolved, and a viscous substance separated. This was dissolved in ether, dried over anhydrous sodium sulphate and the ether evaporated, when we obtained the malonic acid as an oil which did not crystallize. This was dissolved in cold, dilute ammonia and the acid precipitated in the form of its disilver salt by addition of an excess of silver nitrate solution. The salt separated as a flocculent precipitate which was washed with a little water and alcohol, and then dried for analysis in a desiccator over sulphuric acid.

Silver determination.

I. 0.1105 gram substance gave 0.0508 gram Ag.

	Calculated for $C_{13}H_{14}O_6Ag_2$.	Found.
Ag	46.3	45.9

γ-Methyl-α-allylbutyrolactone-α-carbonylthiourea,

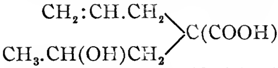
$$\begin{array}{l} CH_3.\underset{|}{CH}.CH_2\underset{|}{C}(CH_2CH:CH_2).CONHCSNH_2 \\ \;\;\;O\text{———}CO \end{array}$$

.—This compound was prepared in a similar manner as the corresponding α-benzyl compound by condensing 10.8 grams of diethyl diallylmalonate with 3.4 grams of thiourea in presence of 2.1 grams of sodium dissolved in 50 cc. of alcohol. After removal of the excess of alcohol, the sodium salt was then dissolved in cold water and the thiourea liberated by addition of dilute sulphuric acid. It separated as a semisolid substance, which finally crystallized. It is desulphurized by digestion in aqueous solution with mercury oxide. The thiourea was purified by crystallization from boiling acetic acid or water, from which it separated in cream-colored plates melting at 134°–135° to an oil. When dissolved in concentrated hydrochloric acid and the solution evaporated to dryness it was recovered unaltered. The compound did not contain water of crystallization.

Nitrogen determinations (Kjeldahl):

	Calculated for $C_{10}H_{14}O_3N_2S$.	Found. I.	II.
N	11.53	11.64	11.59

β-Hydroxypropylallylmalonic Acid,



$$\left.\begin{matrix}CH_2{:}CH.CH_2 \\ CH_3.CH(OH)CH_2\end{matrix}\right\rangle C(COOH)_2.$$

—Two grams of the above thiourea were saponified by heating with 8 cc. of 50 per cent. potash for 2 hours at 130°–150°. Ammonia was observed when the tube was opened and hydrogen sulphide was evolved when the solution was acidified at a low termperature with hydrochloric acid. The malonic acid separated as an oil which we extracted with ether and dried over sodium sulphate. When the ether was evaporated at ordinary temperature the acid was obtained as a thick, viscous oil which soon crystallized in colorless rosettes of small prisms. It is very soluble in alcohol and hot benzene and insoluble in cold water. It melts at 120°–122° with effervescence. It gave no test for sulphur.

Silver Salt.—The acid dissolved immediately in dilute ammonia. On addition of an excess of silver nitrate the silver salt deposited and was washed with water and alcohol. It was dried over sulphuric acid. Silver determination:

I. 0.2623 gram substance gave 0.1379 gram Ag.

	Calculated for $C_9H_{12}O_5Ag_2$.	Found.
Ag	51.92	52.5

New Haven, Conn.,
Jan. 1, 1911.

[Contributions from the Sheffield Laboratory of Yale University.]

CXC.—ON HYDANTOINS: A SYNTHESIS OF PHENYLALANINE AND OF TYROSINE.

By Henry L. Wheeler and Charles Hoffman.

[FIRST PAPER.]

It has been known for a number of years that certain compounds containing the grouping —$HNCH_2CO$— are capable of condensing with aldehydes.

Plöchl,[1] applying Perkin's synthesis to hippuric acid, $C_6H_5CONHCH_2COOH$, found that it condenses with benzaldehyde and salicylaldehyde,[2] and Hofmann[3] showed that this acid condenses with pyruvic acid, but it was Erlenmeyer, Jr.,[4] who gave the correct explanation of the nature of the condensation products which are formed in these reactions. The latter also showed that hippuric acid condenses, in the presence of acetic anhydride and anhydrous sodium acetate, with a number of other aldehydes[5] and also with ethyl formate.[6] From these results and the fact that glycine,[7] H_2NCH_2COOH, was found to condense with aldehydes, Erlenmeyer developed his important syntheses of amino acids, notably tyrosine,[8] phenylalanine,[9] serine,[9] cystine,[9] leucine,[9] etc.

The preparation of tyrosine, which previously had been synthetically obtained only by a more laborious method,[10] was shortened to four operations as follows: The *p*-hydroxybenzaldehyde condensation product of hippuric acid, an azolactone (yield, 85 per cent.) was hydrolyzed to benzoylamino-*p*-hydroxycinnamic acid by warming with alkali, and this

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[1] Ber. d. chem. Ges., **16,** 2815 (1883).

[2] Plöchl and Wolfrum: *Ibid.*, **18,** 1183 (1885).

[3] *Ibid.*, **19,** 2554 (1886).

[4] Ann. Chem. (Liebig), **271,** 137 (1892); **275,** 1 (1893). Erlenmeyer and Stadlin: *Ibid.*, **337,** 283, 265. Erlenmeyer and Arbenz: *Ibid.*, **337,** 302 (1904).

[5] Erlenmeyer: Ann. Chem. (Liebig), **307,** 70 (1899). Erlenmeyer, with Bade, Mattes, Stadlin and Wittenberg: *Ibid.*, **337,** 205, 222, 265, 271, 283, 294 (1904).

[6] Erlenmeyer and Stoop: *Ibid.*, **337,** 236.

[7] Ber. d. chem. Ges., **25,** 3445 (1892). Erlenmeyer and Früstuck: Ann. Chem. (Liebig), **284,** 36 (1895).

[8] Ber. d. chem. Ges., **30,** 2981 (1897). Erlenmeyer and Halsey: Ann. Chem. (Liebig), **307,** 138 (1899).

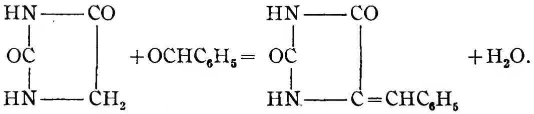
[9] With Kunlin: *Ibid.*, **307,** 146 (1899); **357,** 236; **316,** 145 (1901).

[10] Erlenmeyer and Lipp: *Ibid.*, **219,** 170 (1883).

in alkaline solution was reduced with sodium amalgam to benzoyltyrosine (yield, 10–15 per cent.), then on heating with hydrochloric acid, tyrosine hydrochloride was obtained (yield, 25 per cent.). The last two operations were later improved by Emil Fischer so that a yield of 65–70 per cent. of benzoyltyrosine was obtained, the benzoyl derivative being hydrolyzed almost quantitatively by boiling with hydrochloric acid.[1]

Erlenmeyer also showed that creatine, $H_2NC(NH)$-$N(CH_3)CH_2COOH$, condenses with benzaldehyde, under the influence of acetic anhydride, giving benzalacetylcreatinine.[2] He then examined phenylglycine, acetylphenylglycine, and phenylhydantoin, but these substances did not condense with benzaldehyde by his method.[3]

With the intention of making a study of various hydantoin derivatives for synthetical purposes, we first examined the behavior of hydantoin itself when heated with aldehydes and we have found that excellent yields of condensation products are obtained when this substance is simply boiled with aldehydes in acetic acid solution and in the presence of anhydrous sodium acetate. The use of acetic anhydride is unnecessary. For example, with benzaldehyde benzalhydantoin is easily obtained in yields of 70–80 per cent. of the calculated. The reaction takes place as follows:



Benzalhydantoin has previously been obtained by a different method. Ruhemann and Cunnington[4] found that phenylpropiolic ester condenses with urea in the presence of sodium ethylate, and Ruhemann and Stapleton[5] showed that this

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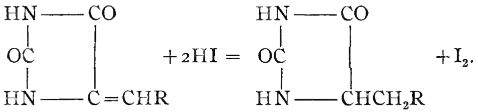
[1] Ber. d. chem. Ges., **32**, 3638 (1900).
[2] Ann. Chem. (Liebig), **284**, 49 (1895).
[3] *Ibid.*, **307**, 73 (1899).
[4] J. Chem. Soc., **75**, 958.
[5] *Ibid.*, **77**, 246 (1900).

product, first supposed to be the ureide of phenylpropiolic acid, is, in fact, benzalhydantoin.

We have also found that the condensation of hydantoin with anisaldehyde, *p*-nitrobenzaldehyde, furfural, piperonaldehyde, salicylaldehyde, and 3,5-dichlor-*p*-hydroxybenzaldehyde takes place in a similar manner to the above and that the yields are excellent.

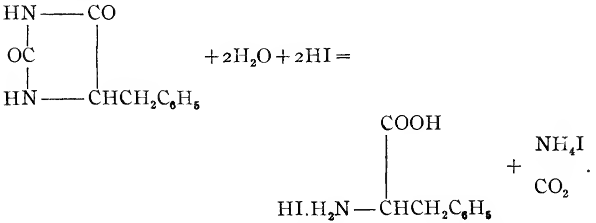
These condensation products would be of only secondary interest if it were not possible to smoothly reduce them to the corresponding hydrated hydantoins and then hydrolyze the products to the amino acids. These results have now been accomplished.

We find that the condensation products on moderate warming with hydriodic acid readily give the saturated hydantoins:

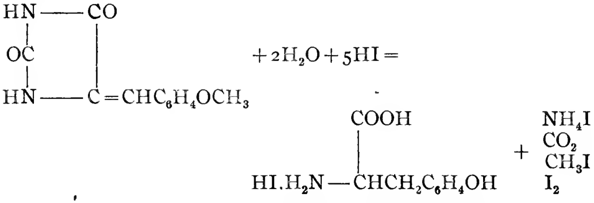


When anisalhydantoin is boiled for a short time with hydriodic acid, *p*-hydroxybenzalhydantoin or tyrosine hydantoin is almost quantitatively obtained.

When the action is more vigorous or when benzalhydantoin or, rather, benzylhydantoin is boiled for a number of hours with hydriodic acid and a little red phosphorus, it is smoothly converted into the hydriodic acid salt of phenylalanine.



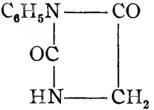
When anisalhydantoin is boiled with hydriodic acid of specific gravity 1.7, a little red phosphorus being added, four steps are combined in one operation: A reduction of the double bond takes place, methyl iodide is evolved, the hydantoin ring is opened and finally the urea grouping undergoes hydrolysis and tyrosine can be practically quantitatively obtained. The reaction may be represented as follows:



$$\begin{array}{ll} \mathrm{HN} & \!\!-\mathrm{CO} \\ | & \;| \\ \mathrm{OC} & \;| \\ | & \;| \\ \mathrm{HN} & \!\!-\mathrm{C}=\mathrm{CHC_6H_4OCH_3} \end{array} + 2\mathrm{H_2O} + 5\mathrm{HI} = \begin{array}{l} \qquad\quad \mathrm{COOH} \\ \qquad\quad | \\ \mathrm{HI.H_2N}-\mathrm{CHCH_2C_6H_4OH} \end{array} + \begin{array}{l} \mathrm{NH_4I} \\ \mathrm{CO_2} \\ \mathrm{CH_3I} \\ \mathrm{I_2} \end{array}$$

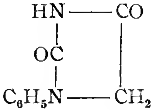
These syntheses of tyrosine and phenylalanine require only two operations, in each case, starting with commercial material.

The tendency of *N*-substituted hydantoins to condense in the above manner with aldehydes has also been examined by us in the case of the following three types of phenylhydantoins:



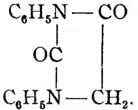
$$\begin{array}{ll} \mathrm{C_6H_5N} & \!\!-\mathrm{CO} \\ | & \;| \\ \mathrm{OC} & \;| \\ | & \;| \\ \mathrm{HN} & \!\!-\mathrm{CH_2} \end{array}$$

I.



$$\begin{array}{ll} \mathrm{HN} & \!\!-\mathrm{CO} \\ | & \;| \\ \mathrm{OC} & \;| \\ | & \;| \\ \mathrm{C_6H_5N} & \!\!-\mathrm{CH_2} \end{array}$$

II.



$$\begin{array}{ll} \mathrm{C_6H_5N} & \!\!-\mathrm{CO} \\ | & \;| \\ \mathrm{OC} & \;| \\ | & \;| \\ \mathrm{C_6H_5N} & \!\!-\mathrm{CH_2}. \end{array}$$

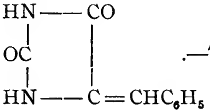
III.

1-Phenylhydantoin (I) condenses with anisaldehyde as readily as the unsubstituted hydantoin. On the other hand, under the same conditions, we obtained no condensation product with either 3-phenylhydantoin (II) or with 1, 3-diphenylhydantoin (III).

We intend later to give an account of the chemical behavior of hydantoin condensation products and the employment of hydantoins in other syntheses.

EXPERIMENTAL PART.

Benzalhydantoin,

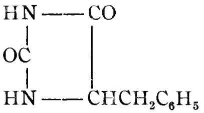


$$\begin{array}{ll} \mathrm{HN} & \!\!-\mathrm{CO} \\ | & \;| \\ \mathrm{OC} & \;| \\ | & \;| \\ \mathrm{HN} & \!\!-\mathrm{C}=\mathrm{CHC_6H_5} \end{array}$$

.—Ten grams of hydantoin, 20 grams of fused sodium acetate, 40 cc. of glacial acetic acid, 10 drops of acetic anhydride and 15 grams of benzaldehyde were mixed and boiled in an oil bath for 3 hours. The reaction was probably complete in much less time. After cooling, water was added to the mixture until no further precipitation occurred. The yellow substance which separated was filtered, washed with water, and dried. It weighed 15.1 grams, or 80 per cent. of the calculated. A duplicate experiment gave a yield of 70 per cent. of the calculated, while another experiment, performed as above, with the exception that only ten grams of fused sodium acetate were used, gave only a 56 per cent. yield of benzalhydantoin. When the condensation product was crystallized from alcohol it gave straw-yellow needles melting at 220°. It agreed with the description of benzalhydantoin given by Ruhemann.[1]

	Calculated for $C_{10}H_8O_2N_2$.	Found.
N	14.89	14.68

4-Benzylhydantoin (*Phenylalaninehydantoin*),



.—Ten grams of benzalhydantoin, 3 grams of red phosphorus and 45 cc. of hydriodic acid of specific gravity about 1.7 were boiled for 45 minutes, the heating being done in an oil bath. The hydriodic acid was then evaporated and the residue was boiled with water and filtered from the excess of red phosphorus. On concentrating the solution 7.4 grams of benzylhydantoin, melting to an oil at 188°–190°, were obtained.

From the mother liquor, after removing the phosphoric acid with barium hydroxide, and the excess of barium by carefully precipitating with sulphuric acid, 1.6 grams of phenylalanine were found to have been formed under the above conditions. 4-Benzylhydantoin crystallizes from alcohol in colorless, flat, lancet-shaped crystals. On slowly cooling it forms

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[1] *Loc. cit.*

prisms. It also crystallizes readily from water and melts at 190° to a clear oil.

	Calculated for $C_{10}H_{10}O_2N_2$.	Found.
N	14.73	14.40

We also obtained this compound when equal weights of potassium cyanate and phenylalanine were dissolved in water, evaporated to a syrup, and the residue warmed with dilute hydrochloric acid. The product melted at 190° without effervescence.

Reduction of Benzalhydantoin with Aluminium Amalgam.—The reduction by this method was not as satisfactory as that by hydriodic acid, owing to the formation of an aluminium compound. Seven and six-tenths grams of benzalhydantoin were dissolved in 100 cc. of water containing 4.5 grams of potassium hydroxide, and aluminium amalgam, prepared from 4 grams of aluminium, was added. Hydrogen was evolved for 3 hours before all the aluminium was used up. The mixture was then boiled and filtered and the warm filtrate was acidified with hydrochloric acid. A flocculent precipitate separated which weighed 4.1 grams. This had no definite melting point, contained aluminium, and could not be crystallized from any solvent. The analytical results were as follows:

	Calculated for $C_{10}H_{12}O_3N_2.3Al(OH)_3$.	Found.
N	6.33	6.45
Al	18.32	17.50

From the filtrate 5 grams of crystalline material were obtained. This proved to be a mixture of benzylhydantoin and benzylhydantoic acid. Upon crystallizing from alcohol the hydantoic acid separated, and on evaporating the filtrate the hydantoin was obtained.

4-Benzylhydantoic Acid (α-Ureido-β-phenylpropionic Acid), $H_2NCONHCH(COOH)CH_2C_6H_5$.—This substance was obtained when the above hydantoin was boiled for a few minutes with dilute sodium hydroxide and then precipitated in the cold with dilute hydrochloric acid. It crystallizes from alcohol in colorless prisms and it melts at the same temperature as the hydantoin, namely, at 190°; it is readily distinguishd from this substance, however, by melting with vigorous effervescence.

	Calculated for $C_{10}H_{12}O_3N_2$.	Found.
N	13.46	13.00

This compound has recently been shown to be formed in the animal body when phenylalanine is injected into the femoral vein of cats.[1] Our material thoroughly agrees with Dakin's description of the substance. We may add that on warming this substance with dilute hydrochloric acid it is converted into the hydantoin.

Action of Hydriodic Acid on 4-Benzylhydantoin.

Preparation of Phenylalanine.—Five grams of benzylhydantoin, 1.5 grams of red phosphorus, 25 cc. of hydriodic acid (specific gravity 1.7) and 6.8 grams of iodine were boiled for five hours in a flask attached to a return condenser.

On evaporating the hydriodic acid and extracting the residue with boiling water and concentrating, 1.2 grams of unaltered benzylhydantoin separated. The filtrate gave, on precipitating with ammonia, 2.1 grams of phenylalanine, melting with effervescence at 262°, and from the mother liquor after removing the phosphoric acid and ammonia with barium hydroxide, 1 gram more of phenylalanine was obtained. In this case 24 per cent. of the original material was recovered unaltered and 71 per cent. was converted into phenylalanine.

	Calculated for $C_9H_{11}O_2N$.	Found.
N	8.48	8.78

Action of Barium Hydroxide on 4-Benzylhydantoin.—Five grams of benzylhydantoin, 33 grams of crystallized barium hydroxide, and 30 cc. of water were boiled for 5 hours in a hard-glass flask attached to a return condenser. Barium carbonate soon separated and ammonia was given off. After extracting the contents of the flask with boiling water and

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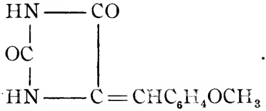
[1] Dakin: J. Biol. Chem., **6**, 241 (1909).

removing the barium by means of carbon dioxide, the solution was concentrated to a volume of about 75 cc. Then, on acidifying with acetic acid and allowing the solution to stand, 1.3 grams of benzylhydantoïc acid separated. The mother liquor was concentrated to a small volume and 3.2 grams of phenylalanine were obtained. In this experiment 23.7 per cent. of the benzylhydantoin was converted into the hydantoic acid and 73 per cent. into phenylalanine. The result, in regard to the preparation of phenylalanine, is practically identical with that obtained on boiling the hydantoin with a saturated solution of hydriodic acid for the same time.

Anisalhydantoin,  .—Ten grams of hydantoin, 20 grams of fused sodium acetate, 40 cc. of glacial acetic acid and 16 grams of freshly distilled anisaldehyde (calculated, 13.6 grams) were mixed in a flask attached to a return condenser and boiled for 2 hours. After cooling, water was added and the product that separated, consisting of almost pure anisalhydantoin, was washed and dried. It weighed 15 grams and with the 0.4 gram obtained from the mother liquor, on concentrating, the yield was 71.5 per cent. of the calculated. Three other experiments, as above, gave 74, 70 and 72 per cent. yields. Varying the time of heating beyond 2 hours and increasing the amount of sodium acetate did not increase the yield.

On evaporating the acetic acid solutions and washings from the crude product with hydrochloric acid, unaltered hydantoin could invariably be extracted with alcohol. In one experiment, therefore, we increased the amount of anisaldehyde to twice the weight of hydantoin employed; the yield was then 69 per cent. of the calculated. Another experiment was performed as above, only that one molecular proportion of acetic anhydride was added. The yield of material then, on adding water, was 64 per cent. and from the mother liquor 12 per cent. more of less pure material was obtained on evaporating the acetic acid.

Attempts to effect a condensation by warming the hydantoin with anisaldehyde in glacial acetic acid or in acetic anhydride, without sodium acetate, gave very little condensation product and the yield was poor when less than two parts by weight (compared to the weight of hydantoin), of fused sodium acetate was used.

Anisalhydantoin is difficultly soluble in boiling water, only moderately soluble in alcohol, and readily soluble in glacial acetic acid. It crystallizes from alcohol in brownish yellow prisms which melt at 243°–244° wth slight effervescence. It dissolves in cold alkali and is precipitated unaltered by acetic or hydrochloric acid; when it is boiled with alkali it gives *p*-methoxyphenylpyruvic acid.

	Calculated for $C_{11}H_{10}O_3N_2$.	Found.
N	12.84	12.63

Bromanisylhydantoin, $C_{11}H_9O_3N_2Br$.—Two grams of anisalhydantoin were suspended in 30 cc. of glacial acetic acid and 1.5 grams of bromine (calculated for 2 atoms) were slowly added. Heat was evolved and the hydantoin went into solution. There was no evidence of hydrobromic acid being liberated until the solution was warmed. The solution was evaporated to dryness on the steam bath, the residue treated with water, washed and dried. It weighed 2.7 grams, which is almost the calculated for a monobrom compound. It is difficultly soluble in water and only moderately soluble in alcohol, from which it crystallizes in clusters of long, light-yellow needles. It melts to an oil at 247°. When gently warmed with an aqueous solution of silver nitrate and nitric acid silver bromide separates.

	Calculated for $C_{11}H_9O_3N_2Br$.	Found.
N	9.43	9.40

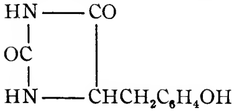
Preparation of Tyrosine.—Five grams of anisalhydantoin, 2 grams of red phosphorus and 25 cc. of hydriodic acid (specific gravity 1.7) were boiled in a flask attached to a return condenser for 4 hours and then 6.8 grams of iodine (calculated for 2 atoms) were added and the boiling continued for 5 hours longer. Iodine vapors were immediately evolved and methyl iodide was noticed in the condenser. After the iodine had disappeared, the methyl iodide was allowed to escape by momentarily disconnecting the condenser. When the heating was discontinued the hydriodic acid was evaporated and the residue was extracted with hot water. On concentrating and cooling no hydantoin separated. The solution was then made alkaline with ammonia and 3.5 grams of tyrosine, melting at about 295°, separated. After the removal of phosphoric acid from the mother liquor by means of barium hydroxide and of the excess of the latter with carbon dioxide and a drop of sulphuric acid, and evaporating, 0.2 gram more tyrosine was obtained. The yield was 89.1 per cent. of the calculated.

	Calculated for $C_9H_{11}O_3N$.	Found.
N	7.73	7.97

In another experiment 5 grams of anisalhydantoin were boiled with 25 cc. of hydriodic acid (specific gravity 1.7) and 1.5 grams of red phosphorus for 6 hours. After evaporating the acid and proceeding as above 1 gram of tyrosinehydantoin separated from the aqueous solution, and from the mother liquor 3.15 grams of tyrosine were obtained. In this experiment 76 per cent. of the material was converted into tyrosine and 20 per cent. into tyrosinehydantoin.

In regard to the melting point, or rather decomposition point, of synthetic tyrosine we wish to state that it is indefinite. On rapidly heating in one case the substance effervesced at 340°, while the other portion of the same preparation melted at 295° when kept in a bath at this temperature for about a minute.

4-p-*Hydroxybenzylhydantoin* (*Tyrosinehydantoin*),



.—Seven and seven-tenths grams of

anisalhydantoin, a little red phosphorus and 35 cc. of hydriodic acid (specific gravity 1.7) were boiled for one hour and then 20 cc. of glacial acetic acid were added. On warming again all the organic material dissolved. The acid was evaporated and the residue was extracted first with boiling water and finally with a little dilute ammonia. On evaporating, 5.7 grams of crystalline material separated, or 79.1 per cent. of the calculated for tyrosine hydantoin. The filtrate gave 0.5 gram more substance, which proved to be tyrosine when it was evaporated to dryness, the residue taken up in a little water, ammonia added, evaporated to dryness again, and the residue treated with dilute acetic acid. Under these conditions 7.8 per cent. of the calculated for tyrosine was obtained.

In another experiment, using the same amount of hydriodic acid, one-half the amount of anisalhydantoin and heating for the same time, the percentage yield of tyrosinehydantoin was about the same, namely, 83 per cent. of the calculated.

Tyrosinehydantoin crystallizes from water in beautiful, small, colorless prisms. It appears to be a little less soluble in alcohol and it melts at 257°–258° to an oil which at first slightly effervesces, then decomposes. It dissolves in alkali and ammonia and it is precipitated by acetic acid as well as hydrochloric acid. It gives an intense Millon reaction.

	Calculated for $C_{10}H_{10}O_3N_2$.	Found.
N	13.59	13.59

Blendermann[1] isolated from the urine of rabbits fed with tyrosine a substance which agreed in analytical results with those calculated for tyrosinehydantoin. The substance, on hydrolysis with baryta, gave tyrosine. Blendermann's substance, however, does not agree in its properties with our tyrosinehydantoin. He describes the substance as crystallizing in yellow needles which, on heating, turn brown at about 270° and then melt at 275°–280°, or 18°–23° higher than our material. It is possible that these differences may

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[1] J. Physiol. Chem., **6**, 253 (1882).

be due to Blendermann's hydantoin being an optically active isomer.

4-p-Hydroxybenzylhydantoic Acid (Tyrosinehydantoic Acid), $H_2NCONHCH(COOH)CH_2C_6H_4OH$.—The hydrolysis of tyrosinehydantoin to the hydantoic acid does not take place as easily or as smoothly as the corresponding reaction in the case of phenylalaninehydantoin and the conditions of solubility are the reverse. In this case the hydantoic acid is more soluble than the hydantoin. It can be prepared by boiling the hydantoin with dilute alkali for a short time. Some ammonia is evolved and on acidifying with acetic acid the unaltered hydantoin is precipitated. On evaporating the filtrate to dryness and acidifying the residue with dilute hydrochloric acid the hydantoic acid is obtained.

Tyrosinehydantoic acid is best prepared from tyrosine and potassium cyanate. This method has previously been used by Jaffe,[1] but, owing either to this method of isolating the substance or to having used impure tyrosine, he obtained an impure product.

Synthetic tyrosine was dissolved in hot water and treated with an equal weight of potassium cyanate in a small amount of water. The solution was then concentrated (to 10 cc. for 1 gram of tyrosine) and hydrochloric acid was added at ordinary temperature. On standing overnight prisms separated which melted with effervescence at 172°. The material was readily soluble in alcohol and water and on recrystallizing the melting point was not changed. When boiled with dilute hydrochloric acid it gives tyrosinehydantoin, melting at 257°–258°.

	Calculated for $C_{10}H_{12}O_4N_2$.	Found.
N	12.50	12.40

Action of Barium Hydroxide on Tyrosinehydantoin.—Four and eight-tenths grams of tyrosinehydantoin, 30 grams of crystalllized barium hydroxide and 30 cc. of water were placed in a flask attached to a return condenser and boiled for 6 hours. The mixture was diluted with water, filtered hot from

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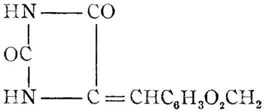
[1] Z. physiol. Chem., **7**, 310 (1882).

the barium carbonate that had been formed, carbon dioxide was passed into the solution, and the solution filtered again and concentrated. On adding acetic acid a snow-white mass of long, slender, silky needles separated. The first crop weighed 2.0 grams and on concentrating 1.35 grams more were obtained. This material melted with effervescence when kept at 295° and proved to be tyrosine. The syrupy mother liquor and the barium carbonate precipitates were dissolved in acetic acid and the barium precipitated by a slight excess of sulphuric acid. On concentrating this solution, finally adding ammonia and acetic acid, 0.7 gram of material separated which, on crystallizing from water, melted at 255° with effervescence and was therefore unaltered hydantoin. The yields were 79.6 per cent. of the calculated of tyrosine and 14.5 per cent. of hydantoin.

Piperonalhydantoin,

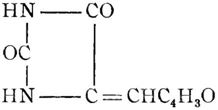


$$\begin{array}{lcl} \mathrm{HN} & — & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & | \\ | & & | \\ \mathrm{HN} & — & \mathrm{C{=}CHC_6H_3O_2CH_2} \end{array}$$

.—Five grams of hydantoin, 8.5 grams piperonal (calculated, 7.5 grams), 20 cc. of glacial acetic acid and 10 grams of fused sodium acetate were boiled, without the addition of acetic anhydride, for 2 hours. On cooling and adding water 10 grams of condensation product were obtained, or 86 per cent. of the calculated. This material was fairly soluble in alcohol and dilute acetic acid and it crystallized in clusters of yellow prisms melting at 245°. It is readily soluble in glacial acetic acid.

	Calculated for $C_{11}H_8O_4N_2$.	Found.
N	1207	11.85

Furfuralhydantoin,

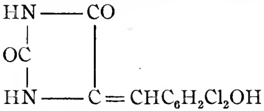


$$\begin{array}{lcl} \mathrm{HN} & — & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & | \\ | & & | \\ \mathrm{HN} & — & \mathrm{C{=}CHC_4H_3O} \end{array}$$

.—Five grams of hydantoin, 10 grams of fused sodium acetate, 6 grams of furfuraldehyde (calculated, 4.8 grams), 20 cc. of glacial acetic acid and no acetic anhydride, were mixed and boiled for 1 hour and 15 minutes. The product, on washing with water and drying, weighed 6.8 grams, or 76 per cent. of the calculated. This was first crystallized from dilute acetic acid and then from alcohol. It formed dark yellow prisms which melted to a dark oil at 232°. When dissolved in concentrated sulphuric acid it gave an intense green color.

	Calculated for $C_8H_6O_3N_2$.	Found.
N	15.73	15.77

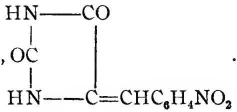
3,5-Dichlor-p-*hydroxybenzalhydantoin*,



.—Thirteen and two-tenths grams 3,5-dichlor-*p*-hydroxybenzaldehyde,[1] 7.5 grams of hydantoin, 15 grams of fused sodium acetate and 35 cc. of glacial acetic acid were boiled for 3.5 hours without the addition of acetic anhydride to the mixture. In two hours a cake of solid material had separated from the hot acetic acid. The contents of the flask, on treating in the usual manner, gave 13.8 grams of condensation product, while the calculated is 18.8 grams. It was every difficultly soluble in alcohol and almost insoluble in boiling water. For analysis it was crystallized from a mixture of acetic acid and alcohol, clusters of light yellow, long, slender needles being obtained. These melted either directly at 300°, with effervescence, or on keeping the substance at this temperature for a short time. It gives an orange ammonium salt, which is difficultly soluble in water. It dissolves readily in alkali.

	Calculated for $C_{10}H_6O_3N_2Cl_2$.	Found.
N	10.25	10.04

p-*Nitrobenzalhydantoin*,



.—Two parts

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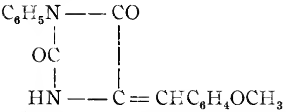
[1] Auwers and Reis: Ber. d. chem. Ges., **29**, 2356 (1896).

of hydantoin, 3 parts of *p*-nitrobenzaldehyde, 3 parts of fused sodium acetate, and 5 parts of glacial acetic acid were mixed and boiled for 1 hour. The condensation product separated as a cake from the hot solution. It was boiled with water and then found to be very slightly soluble in organic solvents. It was crystallized from a large volume of water for analysis, whereupon it formed lemon-yellow prisms melting at 254° with decomposition.

	Calculated for $C_{10}H_7O_4N_3$.	Found.
N	18.02	17.85

When this hydantoin is dissolved in normal potassium hydroxide it gives a blood-red solution.

1-Phenylanisalhydantoin, .—



Five grams of 1-phenylhydantoin, 6 grams anisaldehyde (calculated, 4 grams), 10 grams of fused sodium acetate, 20 cc. of glacial acetic acid and a few drops of acetic anhydride were mixed and boiled for 2.5 hours. On treating in the usual manner 6.7 grams of condensation product were obtained, or 80 per cent. of the calculated. It was almost insoluble in hot water and difficultly soluble in alcohol. It crystallized from the latter solvent in small, yellow prisms, which melted to a brown oil at 251° without decomposition. On cooling and heating again it remelted at the same temperature.

	Calculated for $C_{17}H_{14}O_3N_2$.	Found.
N	9.52	9.67

When 3-phenylhydantoin and 1,3-diphenylhydantoin were treated precisely as in the above case nothing but unaltered material was obtained.

3-Phenylhydantoin was prepared from chloracetylurethane and aniline according to the directions of Frerichs and Beckurts.[1] 1,3-Diphenylhydantoin was obtained by a new method.

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[1] Arch. Pharm., **237**, 337.

Phenyl isocyanate was mixed with phenylglycine in approximately molecular proportions, when on gently warming a reaction suddenly started that required cooling. The product was dissolved by warming with dilute alkali, filtered from some insoluble material, and precipitated by hydrochloric acid. This apparently gave the hydantoic acid melting at 195° with effervescence. When this was dissolved in hot alcohol with the addition of a little hydrochloric acid and allowed to crystallize, the diphenylhydantoin described by Bischoff and Hansdörfer[1] was obtained. It formed almost colorless plates melting at 137°. The plates or spangles had the striking property of reflecting all colors of the rainbow on separating from an alcoholic solution.

NEW HAVEN, CONN.,
December. 1910.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[2]

PART III. THE REGULATION OF TEMPERATURE.

BY H. N. MORSE, W. W. HOLLAND, AND E. G. ZIES.

When the last work at 0° was done in 1906–1907,[3] the low temperature was secured by pumping water continuously over broken ice and around the metallic cans in which the cells were located. The temperature which was obtained in this way was not 0°, but was always somewhat higher. As a rule, it varied between 0°.15 and 0°.30. The maximum variation from the beginning of the work to the end was between 0°.12 and 0°.38. The temperature in the air space above the cells in which the manometers were located was always higher and much more variable. Such fluctuations in temperature are capable of producing very large *thermometer effects*. It was, therefore, determined, before beginning the

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[1] Ber. d. chem. Ges., **25**, 2274 (1892).

[2] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers which have preceded the present one will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 137; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257; **45**, 91 and 237.

[3] THIS JOURNAL, **37**, 425.

more elaborate attempts to ascertain the relation of osmotic pressure to temperature, to devise, if possible, some means of maintaining the cells *at o°* as exactly and continuously as we were able to maintain them at any higher temperature. The arrangement which was finally evolved for the purpose is shown in Figs. I, II and III. The apparatus, which is made of galvanized iron, consists of three principal parts: First, a can *A*, in which the cells are placed; second, a much larger one *B*, in which *A* is suspended by means of the arrangement shown in Fig. II; and third, the cylinder *C*, which shuts down tightly upon *B*. There is an enclosed chamber, *e*, running through the whole length of *C* and open at both ends, in which are located the upper ends of the manometers, and the two thermometers which are shown in the figure. The thermometers and manometers are exposed to view, when a reading is to be made, by opening the felt-lined door, *f*. In order that the door may be opened and closed from the outside, the detachable rod, *g*, by which the door is opened and shut, is made to extend through the top of the larger bath which surrounds *A*, *B* and *C*. The bottoms of both *A* and *B* are perforated, so that no water can collect in the cans.

The "larger bath," referred to above, is one of those ordinarily used for the measurement of pressure at higher temperatures. To prepare it for work at o°, it is emptied, and the circulating pipes, including the pump, are removed, leaving the copper-lined tank entirely empty. On the bottom of this, in the center, is placed a staging about 5 cm. high, on which rests the ice-filled arrangement consisting of *A*, *B* and *C*. All the space in the tank which is not occupied by *A*, *B* and *C* is filled with closely packed broken ice, and the water which collects upon the bottom is removed by means of an automatic siphon. All the space in the upper part of the bath—usually designated as the "air space"— which is not occupied by the upper part of *C* is filled with ice containers of such form that *C* is surrounded by them, except in front of the door, *f*. One of these occupies the space between the upper end of *C* and the top of the outer bath, the upper end of the chamber *e* being covered to prevent the entrance of water.

All the ice containers in the air space above are open at the lower end, so that the broken ice moves constantly downwards as it melts away underneath, keeping the tank below and also the can *B* always full. A little over 300 kilograms of ice are required to fill the bath properly, and the amount of fresh ice which it is necessary to introduce at the top daily is between 20 and 25 kilograms.

The ice container above *C* and *C* itself, after picking out the ice in them, can be lifted through the opened top of the bath, whenever cells are to be removed from *A*. If cells are to be introduced, all parts of the bath except *C* and the containers above it are closely packed with ice, and, after waiting until the temperature in *A* has fallen to 0°, the cells are placed in position. *C* is brought down upon *B* and packed with ice. Finally, the container which belongs directly above *C* is placed in position and filled with ice.

The arrangement described above served its purpose perfectly. The temperature in *A* did not deviate sensibly from 0° during the entire work, and for the first and the last time, we were nearly free from *thermometer effects*. The temperature in the manometer space, *e*, was less satisfactory. It appeared to vary from 0° to 0°.3, but this is believed to have been due to the lamp which was used in reading, more than to any inability on the part of the arrangements to maintain a temperature of zero in the space occupied by the manometers. We had not then adopted the plan of screening the light with a solution of nickel sulphate, which was afterwards found to reduce the heating effects of the lamp by about 99 per cent.

The complete system for the regulation of temperatures above 0° is shown in Fig. IV. It consists of a relay, *R*; two condensers of large capacity, *C* and C_1; a stove, *s*; a thermostat, *T*; a single battery cell, *B*; and two lamps, *l* and l_1. The different parts can, of course, have any convenient location whatever. The stove circuit (110 volts) begins at the point marked +, passes through the binding posts of the "local" on the relay, thence through the stove and out again. If the circuit is broken between the binding posts, the current passes through the lamp, *l*, thence through the stove and out. In other words, the breaking of the circuit between the relay posts throws the lamp into series with the stove, cutting down the current. All sparking between the platinum points of the relay is prevented by the condenser *C*, which is likewise discharged through the lamp *l*.

The circuit from the battery, *B*, leaving from the point marked +, passes around one side of the condenser, *C*, through the "main line" posts of the relay, *R*, to the other side of the condenser, *C*, thence through the thermostat, *T*, back to the battery. Sparking in the thermostat is prevented by the condenser, *C*. In this system some current passes through the stove all of the time, but the amount which may pass, when the relay circuit is open, can be regulated within wide limits by a proper selection of lamps for the socket, *l*.

It has been stated elsewhere that we use lamps as stoves, for the reason that they heat up and cool down more quickly, and are more convenient, than other electrical heating devices. But we use no lamps of over 50 candle power. If a temperature much above that of the air is to be maintained, the greater part of the heating is done by gas burners or stoves, only so much of the work being left to the electrical devices as may be necessary for purposes of regulation.

The elaboration of the general scheme to which all of the baths now conform was well advanced when the present work was taken up, and we were able at the close of 1908[1] to state the principle on which they are constructed and to illustrate its application to one type of bath. Since then, it has been applied in every detail to two other types of bath. The principle in question was stated as follows: "*If the water in any bath is made to pass rapidly (1) over a continuously cooled surface, then (2) over a heated surface which is more efficient, but which is under the control of a thermostat, and (3) again over the cooling surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set; and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the*

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[1] THIS JOURNAL, **41**, 106.

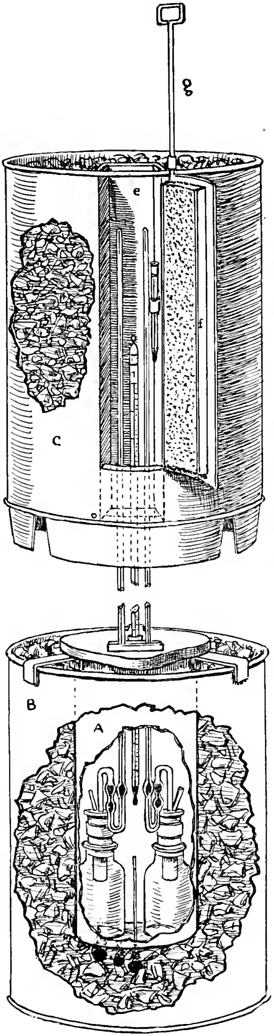

Fig. I.

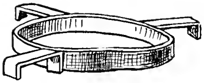

Fig. II.

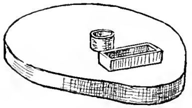

Fig. III.

water. The principle is a general one and provides for the maintenance of any temperature between 0° and the boiling point of water. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid either in the work of the cooling surface or in that of the heating surface."

The three types of baths in use are (1) the baths for general purposes, which are employed intermittently, as occasion arises; (2) those in which the membranes are deposited, and the solutions are maintained at constant temperature, which are always "at temperature" while the work is in progress; and (3) the baths in which osmotic pressure is measured, which are also always "at temperature." The first type has been explained in an earlier paper, but not the other two. Types II and III will, however, be more readily understood if the description of them is preceded by a brief account of type I. For this reason, and for the sake of completeness, we shall venture to reproduce some of the figures which appeared in the earlier paper, and to repeat some of the explanations which accompanied them.

Type I.

The various parts of the bath which was first developed on the principle previously stated, are shown in Figs. V to XI, inclusive. "Fig. V represents a cross section of a galvanized iron bath holding about 60 liters. It rests upon the wooden base *a a*, which is raised above the table by the blocks and rubber pieces *b b*, and is surrounded by the thick hair-pad *c c*. Inverted over a hole in the center, and riveted and soldered to the bottom of the bath, is the cylinder *d d d*, which serves as a receptacle for the lamp *e*, or any other suitable kind of electrical heating device. The hole in the wooden base, *a a*, is slightly larger than in the bottom of the bath, and into this is fitted the block *f*, on which is fastened the lamp base, *g*, and the lamp guard, *h h*. The lamp block is held in its place by buttons screwed to the bottom of the wooden base.

"Resting upon the framework, *i i* (Fig. V) and *i i i* (Fig. VI), is the continuous block-tin pipe, *j j j j*, through which the hydrant water circulates. This furnishes the 'cooling surface' previously referred to. The running water enters the bath at *k* and leaves it at *l*. The course of the water in the pipe, after entering the bath, is continuously horizontal or upward—never downward. This arrangement is necessary in order to prevent the lodgment of air in any part of the pipe. The plan of the continuous tin pipe and of the frame on which it rests is seen in Fig. VI. The successive coils of the pipe (six in number) are separated by the pegs seen in Figs. V and VI, and on these rests the galvanized iron disc *m m*. The hood *n n* shuts down tightly over a flange on the disc, *m m*, and is secured in its place by means of set screws directed towards *d d*. The form of the hood will be clear from the figure, and it is necessary only to call attention to the pin holes, for the escape of air, at *o o*, and to the larger holes at *p p*, through which a portion of the water raised by the propeller, *r*, escapes into the outer bath.

"The propeller, *r*, is revolved at any required speed by a smooth porpoise-hide belt, six mm. in width, which is passed around the pulley *s*, and over the pulley of a small motor located at some distance from the bath. The thermostat is seen at *u*, and the thermometer at *v*. The supports for both are clamped to the rim of the bath, as is also the adjustable support, *w w*, for the propeller and its accessories.

"It is quite essential that the hydrant water flowing through the pipe in the bath shall be under a constant pressure, otherwise much water and heat are necessarily wasted. The arrangement by which the constant pressure is secured is shown in Fig. VII. It consists of a large standpipe *a* with an overflow *b* near the top. The water from the tap enters at the bottom and passes to the bath through *c*, where the flow is controlled by a stopcock. The circulating water is thus brought under an invariable pressure and it is possible to regulate the quantity passing through the bath with great exactness and for long periods.

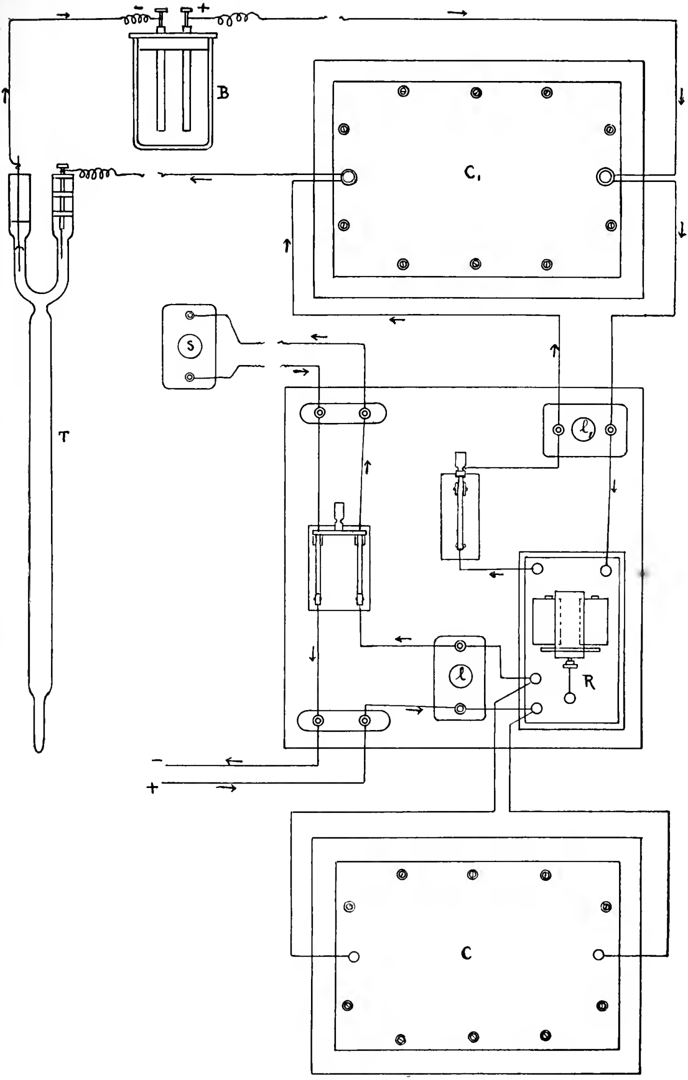

Fig. IV.

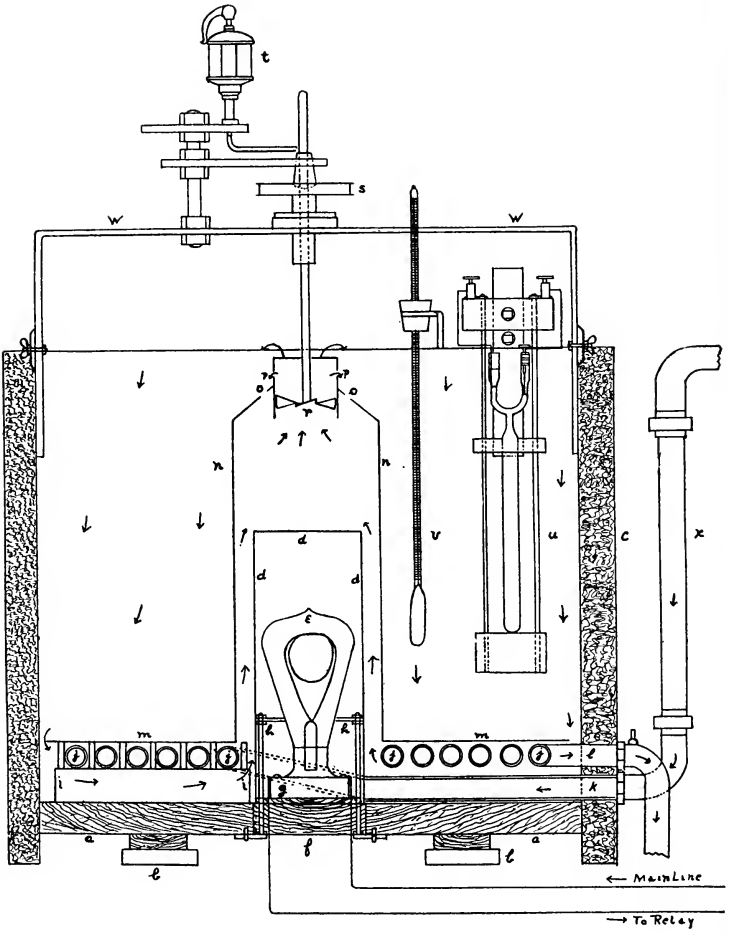
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Fig V

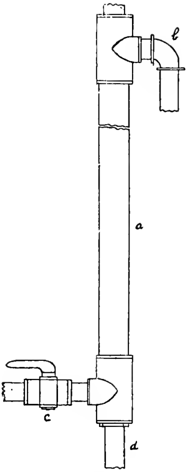


Fig. VII.

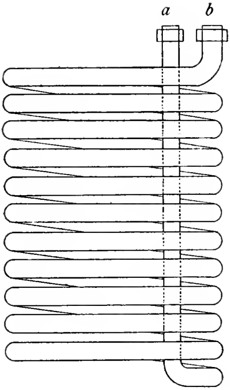


Fig. VIII.

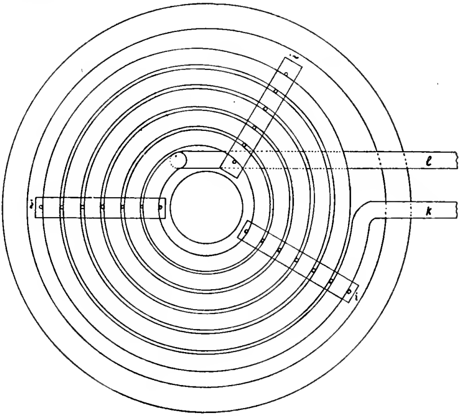


Fig. VI.

"It frequently happens that the temperature of the hydrant water is higher than that at which it is desired to maintain the bath. In such cases, the section of pipe *x*, Fig. V, is removed and replaced by another leading to the coil of block-tin pipe seen in Fig. VIII. The water enters the coil at *a* (Fig. VIII) and passes out of it at *b* into the bath. To cool the hydrant water before it enters the bath, the large and well-protected box in which the coil is located is filled with ice. With the aid of the coil, surrounded by ice, it is practicable to maintain quite low temperatures in the warmest weather.

"It remains to explain the electrical arrangements for heating the water in the bath. It is important that the metallic surface, *d d d* (Fig. V), over which the water passes in its upward course through the hood, shall be quickly heated and readily cooled; hence all unnecessary material in the space heated by the stove is to be avoided, and the stove itself should be of the lightest kind. For this reason, lamps have been preferred to any other variety of electrical heating device. Another great advantage to be gained by the use of lamps is the ease with which, by the selection of lamps with different candle power, the capacity of the stove is suited to the work to be done, i. e., to the temperature to be maintained in the bath.

"The arrangement for the regulation of the heater (*e*, Fig. V) by the thermostat (*u*, Fig. V) is shown in Fig. IX.

"The thermostat is shown separately in Fig. X. The tube containing the mercury is made larger or smaller, according to the degree of sensitiveness which is required of the instrument. It is also drawn out at the lower end into a smaller tube, which may be broken off and afterwards resealed if it becomes necessary to remove the mercury and cleanse the glass. The narrow tubes in the upper part of the instrument are also varied in diameter according to the requirements of the work. The instrument is filled with mercury until it enters the widened portion of the two tubes at the top. The end of a platinum wire is buried to a considerable depth in the mercury in one tube, and on the top of the mercury a quantity of dry shellac is placed. The shellac is melted, and diminished pressure is applied at the other outlet until the mercury, followed by the molten shellac, recedes well into the narrower portion of the tube, when the shellac is allowed to cool and solidify. The other tube at the top is provided with an adjustable platinum wire, the function of which is sufficiently obvious.

"A thermostat of the form just described has the advantage that all of the mercury in the instrument can be submerged in the water of the bath, while the arrangement for adjustment remains above the surface of the water. But the range of temperatures through which it can be used with a fixed quantity of mercury is small. That is, the quantity of mercury must be regulated with reference to the temperature which is to be maintained. This, however, gives very little trouble. If a thermostat is to be employed to maintain a bath at some particular temperature, e. g., 25°, it is plunged—after removing the adjusting screw—into a bath having a slightly higher temperature, and whatever mercury ascends into the wider portions of the tube is removed by means of a very fine pipette. On the other hand, if the mercury recedes too far into the narrow tube, more is added.

"Fig. XI represents the support for flasks, etc., which is used in the bath. It is clamped to the rim of the bath, and, as will be seen from the figure, it can be depressed to any required depth in the water. The bottom is perforated to permit the rapid passage of water. Each bath of the size represented in Fig. V will accommodate five such supports in addition to the thermostat and thermometer.

"The use of the bath is very simple. The thermostat is adjusted to close the circuit at the temperature at which the bath is to be maintained. The bath is brought nearly to that temperature by means of hot water, or ice, or by passing a current of hydrant water through the coiled pipe in the bottom. The flow of hydrant water—cooled, if necessary, by first passing it through the ice coils (Fig. VIII)—is then so regulated that it will very slowly lower the temperature of the circulating water in the bath. The rate of the lower-

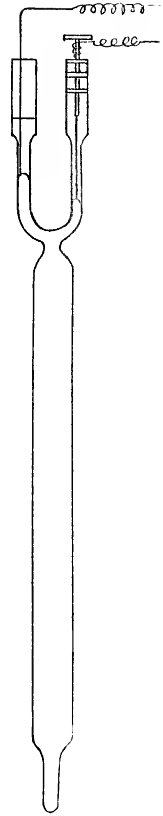


Fig. X.

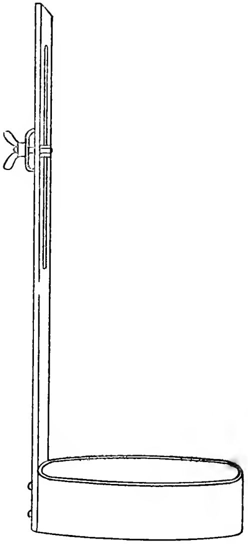


Fig. XI.

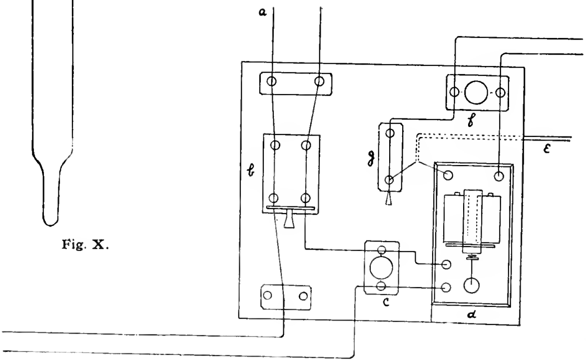


Fig IX.

ing need not exceed 0°.25 per hour, and it should be, for reasons of economy, as small as it is possible to make it. The lamp which is employed as a heater is selected with reference to the temperature to be maintained. It is only necessary that it shall be able, by burning all the time, to raise the temperature of the bath somewhat faster than the running hydrant water is able to lower it. The thermostat will then permit the lamp to burn only as much of the time as is necessary to maintain the temperature for which the instrument is set.

"The water, as it reaches the top of the hood, after passing over the heating surface, is symmetrically distributed towards all sides of the bath, giving a uniformity of temperature throughout the bath which is very satisfactory.

"The maintenance of any temperature from a little above 0° to that of the room can be readily accomplished by means of the hydrant water, with or without ice. If, however, a temperature above that of the room is to be maintained, the flow of the hydrant water is cut off. The outer surface of the bath and the free surface of the water then becomes the 'cooled' surface, and the bath works on precisely the same principle as when hydrant water is made to circulate through the tin pipe in the bottom. If a temperature above 50° is to be maintained, the consumption of electrical energy becomes expensive in large baths, and it is well to accomplish a portion of the heating by other means. This is done in various ways, the simplest of which is to remove the wooden base and place a gas stove under the bath, taking care so to regulate the quantity of burning gas that the stove *alone* cannot raise the temperature of the bath to the required height. It is only the remainder of the work which is then accomplished by the electrical heater. Another method of economizing electrical energy, when high temperatures are to be maintained, is to cause hot water to circulate through the pipe in the bottom of the bath."

Type II.

Fig. XII represents one of the baths in which the membranes are deposited, and the cells and solutions are maintained at constant temperature. The "*cooled surface*" is furnished by the 8 brass pipes, 1 to 8. The hydrant water, cooled by ice if necessary, enters pipe 1 at the end of the bath and leaves by pipe 8, circulating through the others in the order in which they are numbered. For all temperatures below the highest temperature of the room, it is necessary to keep some cold water in circulation through this system of pipes. The amount which is sent through will, of course, depend on the difference between the temperature of the hydrant water and that which is to be maintained in the bath. It is only necessary that the cooling surface shall be capable of carrying the temperature of the bath a *very little* below that which is to be maintained. Any larger consumption of the hydrant water is useless and wasteful of heat. The external arrangements are precisely like those of baths of type I. If the hydrant water is to be cooled before entering the bath, as when a low temperature, e. g., 5°, is to be maintained in summer, it is passed through the coil shown in Fig. VIII, which is surrounded by ice. The arrangement shown in Fig. VII is also employed to secure a constant pressure upon the circulating water. A word of caution regarding the valves to be used, when a constant pressure is to be maintained, may be of use to others. All of our pressure arrangements were constructed, in the first instance, in accordance with correct principles, so far as we knew; but it was found that they *would not* maintain constant pressure. The flow of water diminished continually, and very small streams ceased altogether after a time. After a long search, the difficulty was located in the valves. Those we were using—the so-called "gate valves"—were found to be so constructed as to permit the accumulation of the gas, which is expelled from water when its temperature is raised, to such an extent as to impede the flow of the water, and to stop it if only a little were passing through the valves. After replacing the "gate valves" by others of the common lever variety, the trouble disappeared.

The "*heating surface*" is furnished by the two copper cylinders 9 and 10, the latter of which is broken in order to show the location of the stoves. The large wooden box is lined with

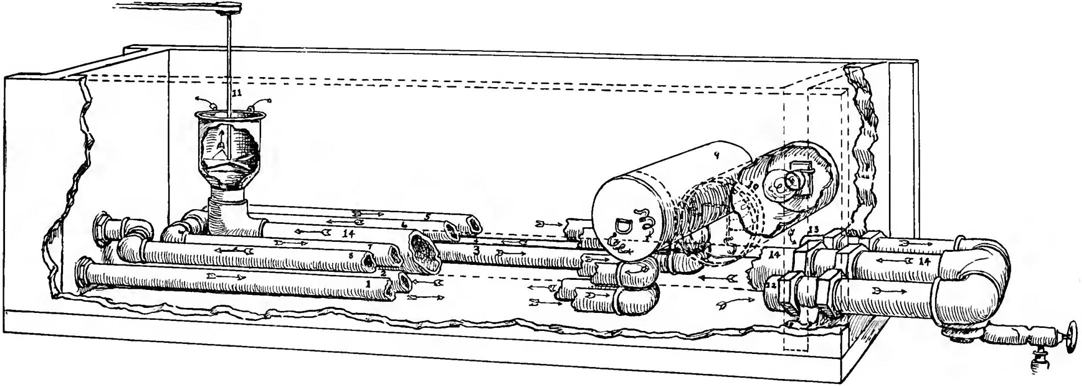


Fig. XII.

copper, and the two copper cylinders in question extend entirely through it, from side to side, and open at both ends on the outside of the bath. They are closed with caps, each of which may or may not carry a lamp. Accommodation is furnished for four lamps, but rarely more than two 32-candle power lamps are in use, even for temperatures of 50° and over. The lamps are regulated according to the scheme which was explained by means of Fig. IV.

The circulation of the water in the bath is effected by means of the pump 11. It enters the two pipes 12 and 13, and passes, in the direction of the arrows, into the large pipe 14, thence to the pump and out again into the open bath. It will be observed that the tendency is to draw the colder water upon the bottom of the bath very rapidly into the pipes 12 and 13, but that, as it enters these, it is necessarily mixed with water which has passed over the "*heated surfaces*" 9 and 10. We have tried many positions in the bath for the heated surface and have found that given in the figure the most satisfactory. The rate of pumping depends on what is found to be necessary in order to secure identical temperatures at the two ends and in the middle of the bath. Ample provision is made for any rate of pumping which may be found to be necessary. A *moderate* rate in some of the larger baths is 400 liters per minute.

The purpose in extending the pipes 12, 13 and 14 outside of the bath is obviously to economize electricity by employing gas for the major part of the heating. The rule here, as in all other baths, is to utilize the latter to the utmost safe limit, leaving for the electrical appliances only so much of the heating as is indispensible for regulation.

Five baths of type II are in use. All of them conform strictly in every particular to the plan given in Fig. XII. All have the standard arrangements for pumping and for electrical heating and regulation, also the arrangement for the circulation of hydrant water, and that for heating the water by gas. Each of the five baths is provided with all the needed accessories for experimental work with the membranes, but no attempt will be made to describe these. Instead, there is introduced a photograph of the baths (Fig. XIII), which will serve to give some idea of their appearance when in use.

Type III.

An example of the baths in which osmotic pressure is measured is shown in Figs. XIV and XV. The first, Fig. XIV, represents the lower part, which is filled with water, and the second, Fig. XV, the upper part, or the "air space." Both compartments are lined with copper and are separated by the vapor-tight brass plate 1, 1, which is divided diagonally across the bath into two parts, which are reunited by the brass strip 2, 2. The brass plate is screwed down upon the upper edge of the outer wooden bath, but between the two there is a strip of rubber. There is also a strip of rubber under the covering plate 2, 2. There are six lead-weighted copper cans suspended from the brass plate, and the flange of each rests upon a rubber collar. Hence, however hot the water in the bath may be, no steam ascends into the upper compartment.

It will be seen that the plan of the lower part of the bath is identical with that of the bath described under "Type II" (Fig. XII). There is in both the same system of pipes (3, 7, 8, etc.) for the circulation of hydrant water, and the same arrangement for pumping the water constantly out of the bath (through 12 and 13), to be heated by gas stoves, and returned through the large pipe—which is numbered 14. There is also in both baths the same provision for the "heated surface," the only difference being that the copper cylinders (9 and 10), in which the lamps are located, are somewhat differently placed.

The copper-lined upper part of the bath (Fig. XV) is the "air space." The electrical heating of this compartment is by means of the shaded lamps 3, 4, 5 and 6. There are two systems of pipes for the circulation of cold or hot water. One of these is located at the top of the bath 7, and is intended for hydrant water only. The other, 8, is situated at one end

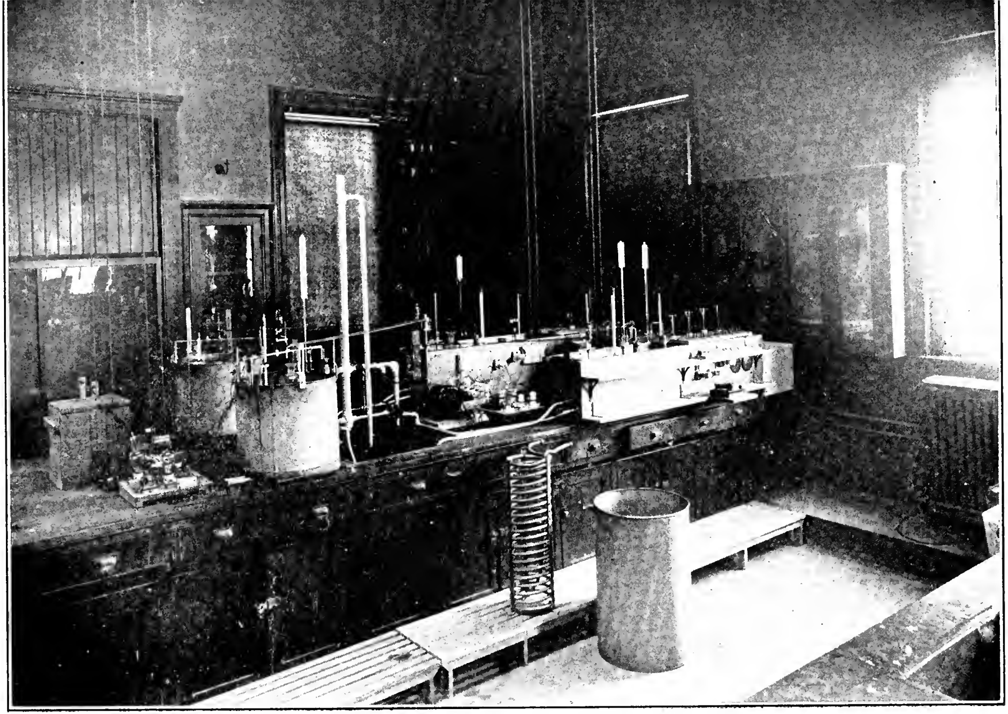


Fig. XIII.

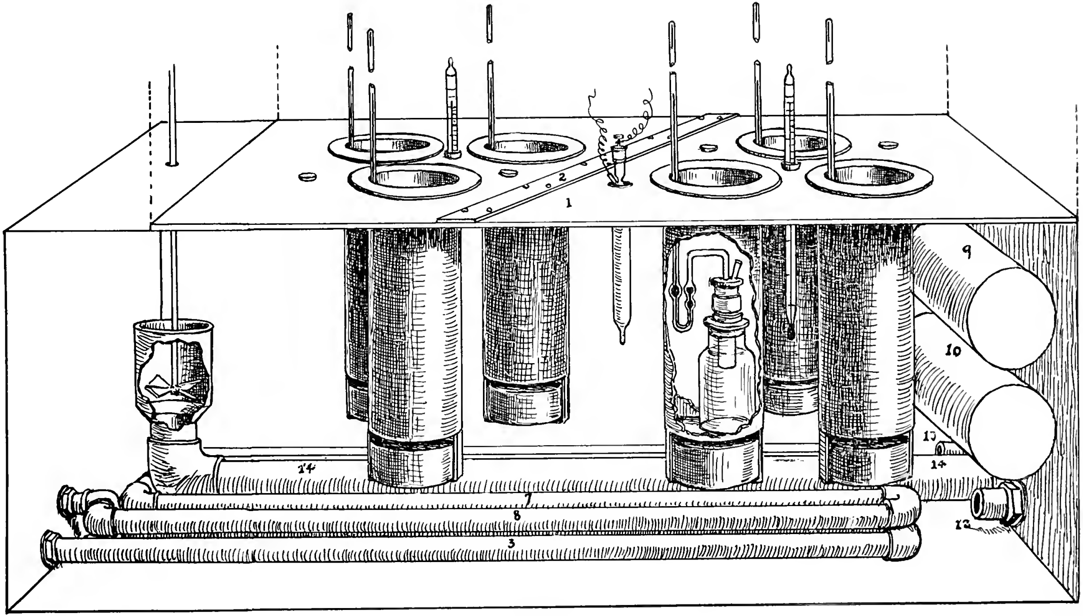
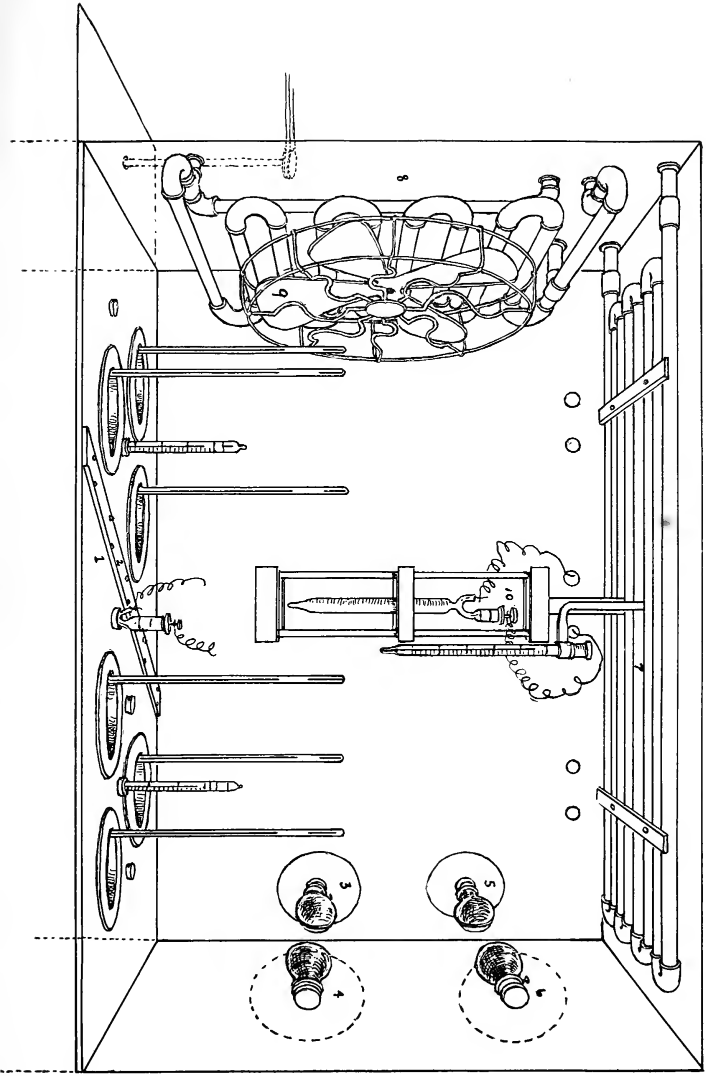


Fig. XIV.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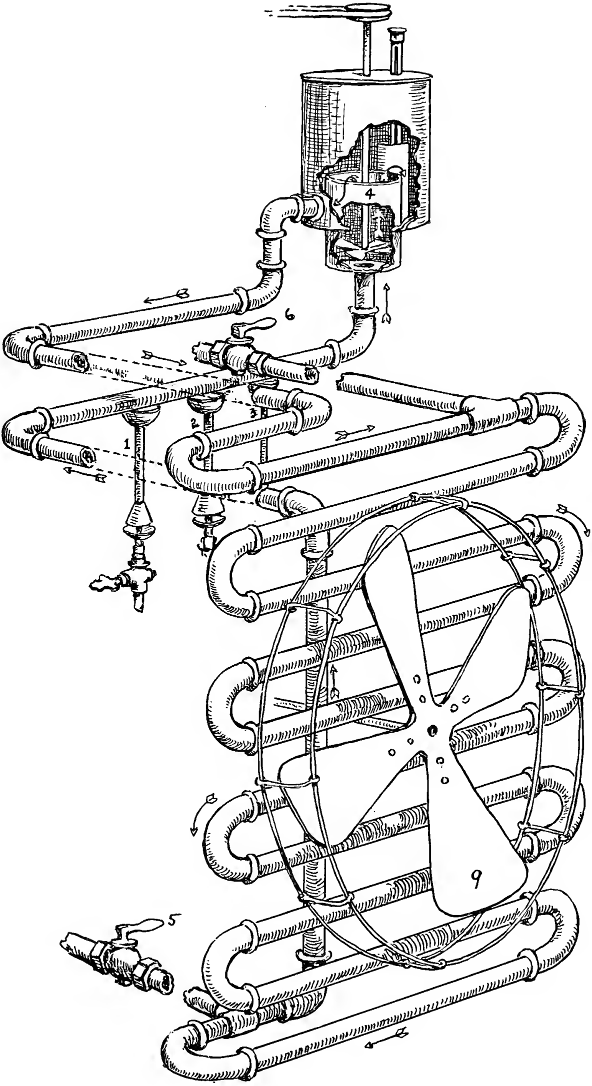

Fig. XVI.

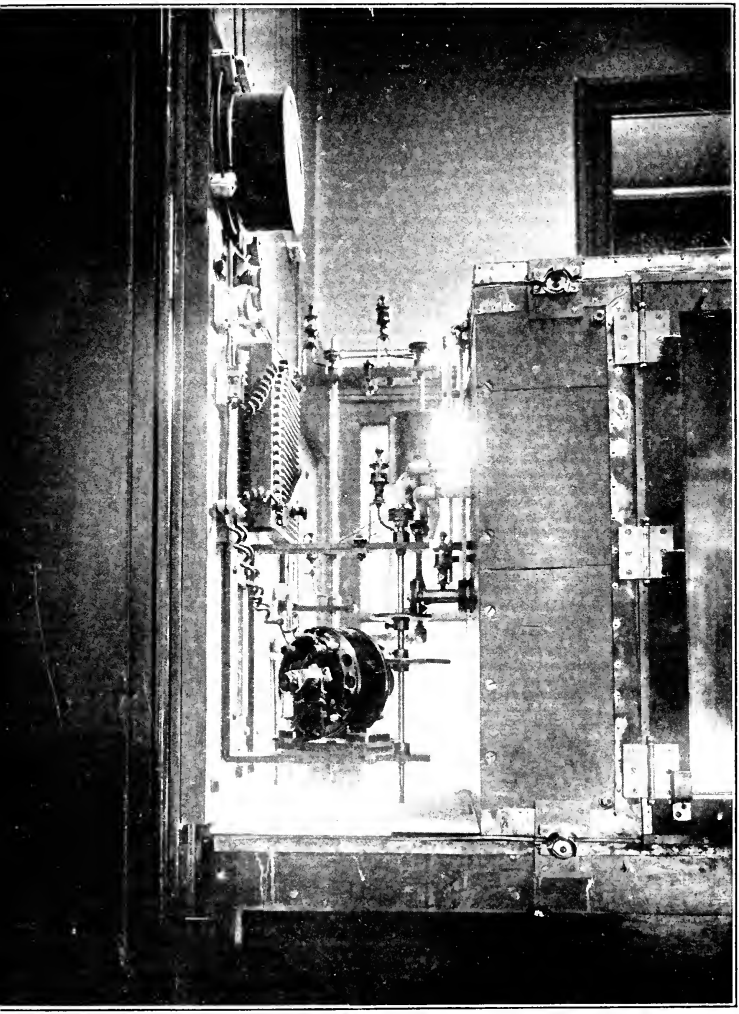

Fig. XVII.

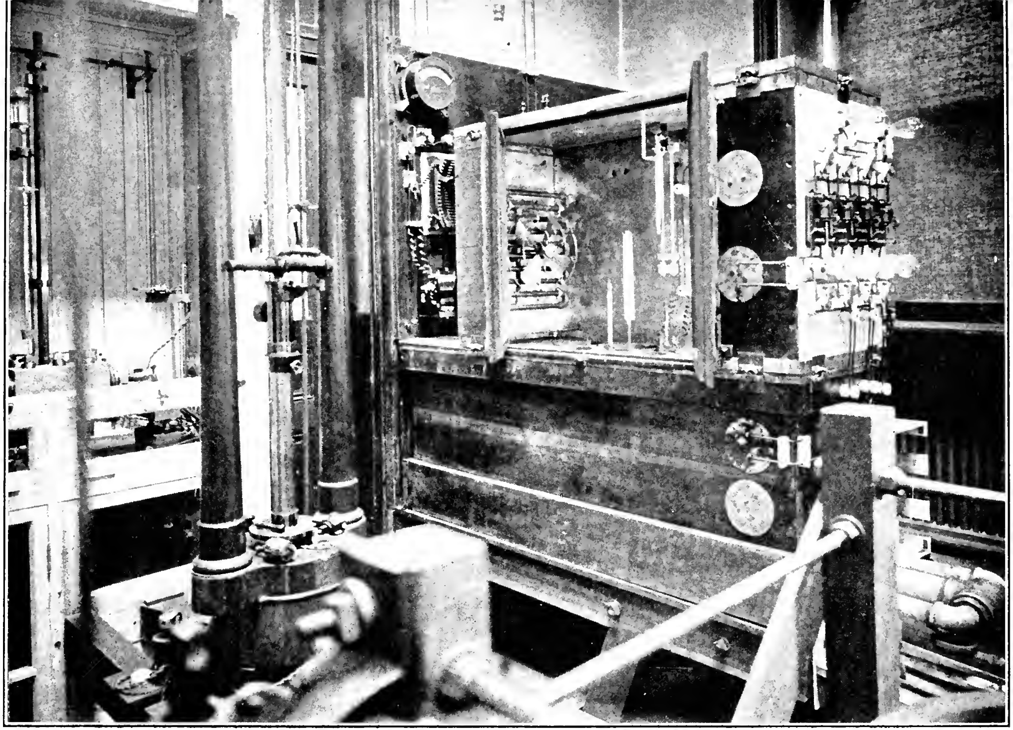

Fig. XVIII.

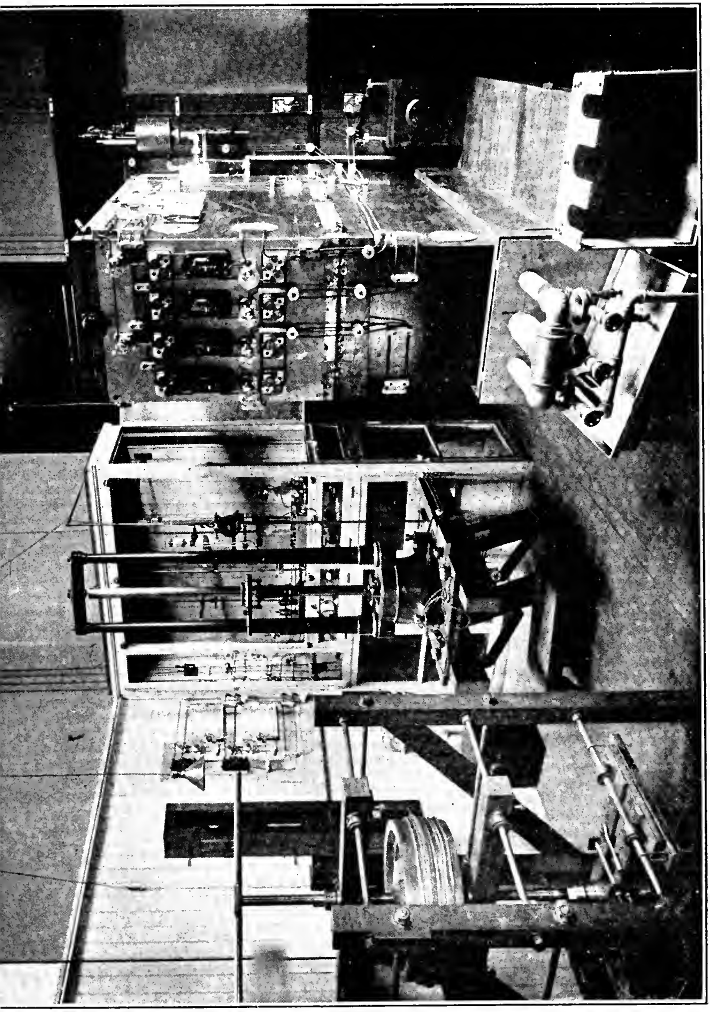

Fig. XIX.

of the bath, and is intended for either hot or cold water, but is used almost exclusively for the former.

The heating and pumping arrangements for the circulation of hot water are situated on the *outside* of the bath. Their relation to what is seen on the inside, 8, Fig. XV, is shown in Fig. XVI. The gas burners, 1, 2, and 3, heat the water on its way to the pump 4. The course of the water in the pipes is made clear by means of the arrows. When the system is used for the circulation of hydrant water, the water enters through the valve 5 and leaves through 6.

The motor fan, 9, Figs. XV and XVI, is employed to keep the air within the enclosed space in constant circulation over the heated pipes. It also serves the important purpose of keeping the manometers gently but constantly agitated, which helps to overcome the tendency of the mercury to lag in the tubes. The agitation can be increased to any desired extent by attaching bits of stiff paper to the tops of the manometers. The water in the pipes is never heated quite high enough to maintain the required temperature, a safe margin being always left to the shaded lamps at the opposite end of the bath, which are under the control of the thermostat 10.

The appearance of the outside of the bath is seen in the photographs, Figs. XVII, XVIII and XIX. Fig. XVII exhibits that portion of Fig. XVI which is exterior to the bath, also that portion of the main pump which is not seen in Fig. XIV. The opposite end of the bath, also the front and a part of the interior, are seen in Fig. XVIII. Fig. XIX gives a view of the back side of the bath and of the end at which are the arrangements for the control of the electrical heating appliances and the heating of the water in the bath by gas. Fig. XIX also includes a view of the "manometer house," and a partial view of the press for the cells.

The bath shown in the photographs is one of three which are employed for the measurement of osmotic pressure. It differs from the other two, not in principle but in that it is used for the higher temperatures. For this reason, the cold water pipes which belong in the top of the bath (7, Fig. XV) are not in position. The others, which are used mainly at temperatures below 35°, are provided with certain accessories which are wanting in the bath seen in Figs. XVII, XVIII and XIX. They are enclosed, and the enclosures, or bath rooms, are supplied with facilities for lowering the temperature outside of the baths. One of these is an extensive system of pipes through which hydrant water can be circulated, either without or with previous cooling by means of ice. Another device, which is useful when low temperatures are required, is an arrangement for pumping outside air, at any desired rate, through the small room in which the bath is located. Formerly it was attempted to maintain the bath room as nearly as possible at the temperature of the bath, but with the present facilities for regulation, this is no longer necessary. As a rule, we now keep the temperature of the bath room about 5° below that of the bath.

JONHS HOPKINS UNIVERSITY,
January 25, 1911.

ON THE EXPERIMENTAL ILLUSTRATION OF THE LAW OF DEFINITE PROPORTIONS THROUGH COMBINATION OF THE HALOGENS WITH FINELY-DIVIDED SILVER.

BY J. H. KASTLE.

It cannot but impress one as somewhat remarkable that, despite the great number of chemists who have, in one way or another, been engaged in the presentation of the fundamental laws of chemical combination in their relation to the atomic theory, there should have been no satisfactory method devised for illustrating experimentally the law of definite proportions. That such is the case, however, can scarcely be controverted. It may be contended, of course, that the proof of this law rests upon all chemical experience and that all known chemical processes serve to establish the truth of this generalization. For those who have a thorough knowledge of chemical science such is undoubtedly true. On the other hand, the beginner in chemistry has no experience with chemical phenomena to draw upon, especially none of quantitative relations. Hence it is that a vastly different proposition confronts the instructor of those beginning the subject of chemistry, who finds imposed upon him the difficult task of imparting to such students a clear and clean-cut notion of the law of definite proportions in its relation to the atomic hypothesis. It has been the writer's experience that but few, if any, simple chemical changes lend themselves well to the experimental illustration of this law.

For a long time, of course, such changes as the conversion of magnesium and copper into their oxides have been employed for this purpose. Thus Tilden[1] suggests the conversion of magnesium into the oxide by heating in air and the conversion of copper into the oxide by decomposition of the nitrate. Newell[2] gives the synthesis of magnesium oxide from the elements and the decomposition of potassium chlorate as experimental illustrations of this law; and Lee[3] makes use of the synthesis of copper oxide, magnesium oxide and iron oxide. Neither of these processes, however, is free from objection. In the case of the oxidation of magnesium loss is apt to occur through volatilization of the metal, and in the case of the oxidation of the copper the direct oxidation proceeds so slowly that too much time is consumed in carrying out the experiment. The attempt has been made to remedy this by first converting the copper into the nitrate by dissolving the metal in nitric acid and decomposing the nitrate by heat. A fundamental objection to this mode of procedure is that the beginner in chemistry may fail to perceive that the black residue left after this operation contains only copper and oxygen. In other words, from the pedagogic standpoint there is a decided disadvantage in having to resort to any indirect chemical process in the experimental illustration of this law, unless the processes are such as to enable us to compare the results obtained by the simple and direct combination of the substances concerned with those reached by the more complicated method of synthesis. In other words, it is not an altogether easy matter to convince a beginner in

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[1] Tilden: Hints on the Teaching of Elementary Chemistry, London and New York, 1896, pp. 13–15.

[2] Newell: Descriptive Chemistry, Boston, 1903, p. 76.

[3] A Text-Book of Experimental Chemistry, Philadelphia, pp. 43–50.

chemistry that 1 gram of copper combines with 0.25 gram of oxygen because 1 gram of the metal yields 1.25 grams of a black substance on solution in nitric acid and decomposition of the resulting compound by heat. If, however, he can also be shown that 1 gram of copper yields 1.25 grams of this same black substance as the result of heating the metal in air or oxygen, the results of the two experiments taken together tend more strongly than either of them alone to convince him that copper always combines with a definite amount of oxygen.

My own experience as a teacher of chemistry has never failed to convince me of the utter futility of attempting to teach chemical theory without suitable laboratory work on the part of the student or careful work upon the lecture table, in which instructor and student participate to as great an extent as possible. I have also never failed to be impressed with the fact that for the experimental illustration of this simplest and most fundamental law of chemical combination, viz., the law of definite proportions, we have no process at all adequate or suitable for the purpose. In this connection it has occurred to me, recently, that perhaps the combination of metallic silver with the halogens might be employed advantageously for this purpose. In its ordinary form, however, silver combines only very slowly with the halogens. Thus, according to Gautier and Charpy,[1] a silver wire lost only 0.54 per cent. of its weight after exposure to dry bromine for four months at 15°. It has recently been observed by Gooch and Perkins,[2] however, that in finely divided form silver combines quantitatively and readily with iodine, and that if the operation be carried out in an atmosphere of hydrogen, electrolytic silver may be employed in the gravimetric determinations of free iodine in aqueous and saline solutions. I have found that finely divided silver combines easily and quantitatively with chlorine, bromine and iodine under ordinary conditions and even when no special precautions are taken to exclude atmospheric air; and that these combina-

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[1] Compt. rend., **113**, 597–600.

[2] Am. J. Sci., **28**, 347. Chem. News, **100**, 308.

tions lend themselves most satisfactorily to the experimental illustration of the law of definite proportions. That such is the case is evident from the following experiments. The finely divided silver employed in these experiments was prepared by the reduction of an ammoniacal solution of silver chloride by means of finely powdered cuprous chloride. When cuprous chloride is added to an ammoniacal solution of silver chloride reduction occurs at once and a finely divided grey deposit or precipitate of metallic silver is produced in a deep indigo-blue liquid. The silver thus precipitated was filtered with the aid of the pump and washed thoroughly with water until all traces of copper were removed. It was then dried in the air bath at 110° to 120° and kept in a desiccator until required for use. Thus obtained, the silver is a uniform grey powder, which in bright light shows a few particles of the glittering metal and under the low powers of the microscope is seen to consist of rounded, grey, spongelike masses, containing only a few glittering specks (probably minute crystals) of the metal. This form of silver combines with the halogens very energetically both when moist and dry. When, for example, it is brought in contact with liquid bromine it combines with it with a hissing noise and when this operation is carried out in the dark a distinct flash of light is observed.

The quantitative determinations were carried out in the following manner: Weighed amounts of the silver powder, from 0.1 to 0.2 gram, were placed in porcelain crucibles. An excess of the halogen (bromine or iodine) was then added and the crucible heated on the water bath until the excess of the halogen had been removed. The crucible was then heated to constant weight in the air bath at 120° to 150°, and then weighed. The mass of silver halide was then fused and weighed again. The increase in weight of the crucible and its contents obviously gives the weight of the halogen with which the given amount of silver has combined. In some of my experiments the silver powder was moistened with water before the addition of the halogen. So far as I have been able to observe, however, water in the liquid state in no way enhances the rapidity of the combination of the silver and halogen and is not essential to the process. The rapidity with which these determinations can be carried out depends, of course, on the quantities of substances started with and on the time consumed in evaporating off the excess of halogen and heating to constant weight in the air bath. In some cases, however, the entire experiment has been completed within an hour. On account of its gaseous nature chlorine has given most trouble in the quantitative determinations, for the reason that it has been difficult to bring an excess of this substance in contact with the silver in a short time. However, even with chlorine good determinations of the conversion of finely divided silver into chloride have been obtained by carrying out the reaction in a porcelain crucible. The mode of procedure is illustrated in the following determinations:

In a porcelain crucible was placed 0.1255 gram of silver powder and 5 cc. of strong chlorine water added. The crucible was then heated gently and a slow current of chlorine passed into the contents of the crucible for 15 to 30 minutes. The crucible was then heated on the water bath and its contents evaporated to dryness. It was then heated to constant weight in the air bath at 120°. The silver chloride thus obtained was found to weigh 0.1503 gram; weight of silver chloride calculated for 0.1255 gram silver, 0.1667 gram. Five cc. of strong chlorine water were then added to the contents of the crucible, which was covered with a watch glass and allowed to stand overnight at ordinary temperature. It was then placed on the water bath and its contents evaporated to dryness. The crucible was dried to constant weight in the air bath at 135°. The silver chloride now weighed 0.1666 gram. This was again treated with 5 cc. of strong chlorine water, evaporated on the water bath and heated to constant weight. The silver chloride now weighed 0.1674 gram and after fusion 0.1667 gram.

In a second experiment 0.1030 gram of silver powder were placed in a porcelain crucible and 15 cc. of strong chlorine water added. The crucible was then covered with a watch glass and placed under a bell jar. After standing overnight the contents of the crucible were evaporated to dryness on the water bath and dried in the air bath at 130° to constant weight. The residue of silver chloride weighed 0.1367 gram; calculated for 0.1030 gram silver, 0.1368. Ten cc. of chlorine water were then added to the residue and the contents of the crucible evaporated to dryness on the water bath. Ten cc. of chlorine were again added to the residue and the contents of the the crucible evaporated to dryness and heated in the air bath to constant weight. The residue now weighed 0.1372 gram. It is possible, therefore, to convert finely divided silver completely into the chloride by a single treatment with chlorine water. It is also always possible to complete the chlorination by successive evaporations with chlorine water, even in those cases in which the first treatment with chlorine fails to convert the silver completely into the chloride. That such is the case is evident from the results of our first experiment. It is also evident from the following: 0.1003 gram of finely divided silver was exposed overnight in a covered porcelain crucible to the action of 10 cc. of the same chlorine water as that used in the preceding experiment. On evaporation to dryness and heating to constant weight the residue was found to weigh 0.1283 gram; calculated for 0.1003 gram silver, 0.1331 gram. Hence, only *85.4* per cent. of the silver had been converted into chloride. After evaporation with a second 10 cc. portion of chlorine water and drying to constant weight the residue was found to weigh 0.1305 gram (92.1 per cent. silver chloride); and after a third treatment with 10 cc. of chlorine water the residue weighed 0.1329 gram (99.4 per cent. silver chloride). After a fourth treatment with 10 cc. of chlorine water it weighed 0.1333 gram and, after fusion, 0.1329 gram.

These results suffice to show that ultimately all of the silver is converted into chloride by the action of chlorine water on the finely divided metal.

The following are the results of the syntheses of the halides of silver from the elements:

No. of experiment.	Silver taken in gram.	Silver halide obtained, in gram.	Quantity of halogen combined with silver, in gram.	Quantity of halogen which theoretically should have combined with silver taken.
1	0.1255	0.1667 AgCl	0.0412 Cl	0.0412 Cl
2	0.1003	0.1329 AgCl	0.0326 Cl	0.0328 Cl
2	0.1030	0.1367 AgCl	0.0337 Cl	0.0338 Cl
3	0.1241	0.2160 AgBr	0.0919 Br	0.0919 Br
4	0.1063	0.1847 AgBr	0.0784 Br	0.0788 Br
5	0.0360	0.0782 AgI	0.0422 I	0.0424 I
6	0.1161	0.2520 AgI	0.1359 I	0.1366 I

It is evident from these results that finely divided silver combines directly with chlorine, bromine and iodine in atomic proportions, and in view of the fact that a considerable excess of the halogen was used in all of these experiments they would serve to indicate to the thoughtful student that in every case metallic silver combines with a definite amount of halogen. By reason of the fact that we can thus synthesize the halides of silver directly from the elements it becomes possible, however, to render these results still more convincing and to put the law of definite proportions before the student, experimentally, in such a way that he cannot escape the conclusion that in the production of the halides of silver definite amounts of the elements are concerned. This is done by synthesizing the halide directly from the elements and then in several other different ways, starting in all cases with finely divided metallic silver. Thus I have prepared the chloride, bromide and iodide of silver, quantitatively, from metallic silver in three distinct ways: (1) by direct combination of the elements; (2) by solution of a known amount of metallic silver in nitric acid and evaporation with the halogen acid; and (3) by the ordinary gravimetric determination of a known amount of silver in solution in nitric acid by precipitation as the chloride, bromide or iodide with the corresponding halogen acid or metallic halide, and filtration of the silver halide on a porcelain Gooch crucible. The following are the results of these determinations:

I. Synthesis of Silver Chloride.

Method of synthesis.[1]	Ag taken in gram.	AgCl obtained, in gram.	Cl in combination with Ag, in gram.	Ratio Ag: Cl (found).	Ratio Ag: Cl (calc. from at. wts.).
(*1*)	0.1255	0.1667	0.0412	1 : 0.3283	1 : 0.3287
(*2*)	0.1255	0.1668	0.0413	1 : 0.3290	
(*3*)	0.1080	0.1433	0.0353	1 : 0.3268	

II. Synthesis of Silver Bromide.

Method of synthesis.	Ag taken, in gram.	AgBr obtained, in gram.	Br in combination with Ag, in gram.	Ratio Ag: Br (found).	Ratio Ag: Br (calc. from atomic wts.).
(*1*)	0.1241	0.2160	0.0919	1 : 0.7405	1 : 0.7408
(*2*)	0.1087	0.1890	0.0803	1 : 0.7397	
(*3*)	0.1066	0.1851	0.0785	1 : 0.7364	

III. Synthesis of Silver Iodide.

Method of synthesis.	Ag taken in gram.	AgI obtained, in gram.	I in combination with Ag in gram.	Ratio Ag: I (found).	Ratio Ag: I (calc. from atomic wts.).
(*1*)	0.0360	0.0782	0.422	1 : 1.1722	1 : 1.1765
(*2*)	0.1003	0.2180	0.1177	1 : 1.1735	
(*3a*)	0.1033	0.2242	0.1209	1 : 1.1704	
(*3b*)	0.1043	0.2263	0.1220	1 : 1.1697	

Reducing these numbers to two places of decimals, it is evident from the above results that under three distinctly different sets of conditions 1 gram of silver combines with 0.33 gram of chlorine, with 0.74 gram of bromine and with 1.17 grams of iodine. It is only logical to conclude, therefore, that silver always combines with definite masses of the halogens, no matter how the combination may be brought about.

UNIVERSITY OF VIRGINIA,
November, 1910.

OBITUARIES.

JACOBUS HENRICUS VAN'T HOFF.

It is with no ordinary feeling of sorrow that we learn of the death of van't Hoff. With him there has passed away one

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[1] In the above table in the syntheses marked (*1*) the halides were made from the elements. In those marked (*2*) they were made by dissolving the silver in nitric acid, adding an excess of the halogen acid and evaporating to dryness in a porcelain crucible. In those marked (*3*) they were made by the usual method of precipitating a known amount of silver dissolved in nitric acid with a metallic halide or halogen acid. In (*3*) under the synthesis of silver chloride, sodium chloride was used; in (*3*) under silver bromide, potassium bromide; in (*3a*) under silver iodide, potassium iodide; and in (*3b*), hydriodic acid.

of the greatest men of science not only of his age, but of all time—a man who found chemistry in a certain state of development, and who left it incomparably more nearly an exact branch of natural science—and these advances were due, directly or indirectly, primarily to the work of van't Hoff.

It is not the intention to give, in this brief notice, a biographical sketch of van't Hoff but to deal mainly with his work. Yet a few matters pertaining to his life should be mentioned. Born in Rotterdam, August 30, 1852, and passing away in Berlin on March 1, 1911, he was in his fifty-ninth year. He was the son of a physician, was trained in the Realschule in Rotterdam, and in the Polytechnicum in Delft, and completed his work at the University of Leiden at the age of twenty. He continued his studies at Bonn under Kekulé, and at Paris under Würtz, and at the age of twenty-two obtained the Doctor's degree at the University of Utrecht. In 1876 he became Privatdozent in physics in the veterinary college in Utrecht. In 1877, he was called to Amsterdam as lecturer in chemistry. In 1878 he became professor of chemistry in the University of Amsterdam, a position which he filled until 1894, when he was called to the University of Berlin, where he remained until his death.

van't Hoff will go down in the history of science primarily as having done three things:

(1) Having founded the science of stereochemistry.

(2) Having applied the law of mass action to chemical reactions, and thus opening up the fields of chemical dynamics and chemical equilibrium.

(3) Having pointed out the close relations between solutions and gases, and thus placing solutions upon a scientific basis.

Let us look more closely into the origin and nature of each of these epoch-making contributions to chemistry.

At the age of twenty-two, when a pupil of Mulder in Utrecht, van't Hoff published, in Dutch, a paper, eleven pages in length, which, he said to the writer only a year and a half ago, gave him as much pleasure to look back upon as any publication that he had ever made.

This paper had to do with the great and, up to that time, apparently hopeless problem of "structural formulae in space." In the following year this was translated into French under the title "La Chimie dans l'Espace."

Wislicenus, two years later, wrote the preface to the translation of this paper into German and saw in it the dawn of a new day for organic chemistry.

From the work of Henri and others, which showed that methane is a symmetrical compound, van't Hoff pointed out that we are forced of mathematical necessity to conclude that methane must be represented in space by the symmetrical tetrahedron, the carbon atom being situated at the center of the tetrahedron and the four hydrogen atoms at the solid angles.

Pasteur had been studying the property possessed by certain substances of rotating the beam of polarized light, and had concluded that in order that a compound should be optically active it must possess some kind of asymmetry. He, however, was unable to point out the kind of asymmetry represented in the molecule. This remained for van't Hoff. He simply extended his theory of the "tetrahedral carbon atom" to that of the "asymmetric tetrahedral carbon atom" or a carbon atom in combination with four different atoms or groups, and the phenomena of optical activity were explained. An examination of all the optically active compounds of carbon then known showed that they all contain at least one carbon atom in combination with four different things, and the same applies to all of the hundreds of optically active compounds of carbon known to-day. Even the terpene derivative which, for a time, was supposed by Baeyer to have no asymmetric carbon atom and which is optically active, has since been shown to contain an asymmetric carbon atom.

This was the beginning of the stereochemistry of carbon, which has led to such brilliant results in the hands of Wislicenus, Baeyer, Hantzsch, Wollach, Fischer and others. Indeed, it is hardly too much to say that stereochemistry has been the philosophy of organic chemistry for the past quarter of a century.

One result of van't Hoff's work with Kekulé and of his study of organic compounds was the writing of his book "Ansichten über die organische Chemie," which he says was written with the view of clearing up his own ideas on the subject. Another result of the influence of Kekulé on van't Hoff and of the latter's interest in organic chemistry was the founding of the science of chemical dynamics and chemical equilibrium.

van't Hoff was impressed with the purely qualitative nature of organic chemistry in that day. Certain substances were brought together under certain conditions, and certain products were formed in determinable quantities—certain "yields" obtained. Little or nothing, however, was done to ascertain quantitatively the velocity with which the reaction in question takes place, the nature of the intermediate products formed, or the conditions when equilibrium is reached. While

Guldberg and Waage were the discoverers of the law of mass action, and applied it to the dynamics of a few chemical reactions, it was van't Hoff who first showed its general applicability to the dynamics and equilibrium of reactions in which compounds of carbon are involved. While these matters were touched upon in his "Ansichten über die organische Chemie," the results of the experimental work of himself, assistants and students, together with their theoretical discussion, were first published in 1884 in his "Etudes de Dynamique Chimique."

In reference to this work Ostwald[1] says: "Hier ist es, wo die Bemühungen unseres Forschers einsetzen, und es ist nichts weniger, als das ganze Gebiet der chemischen Dynamik, die Lehre von der Geschwindigkeit wie die vom chemischen Gleichgewicht, deren systematischen Aufbau er unternimmt. . . . Der Ansatz der Grundgleichungen für die Kinetik und das Gleichgewicht erfolgt wesentlich auf dem Boden der Molekularhypothese, und es werden die mono-, di- und trimolekularen Reaktionen unterschieden. Dies geschieht im Gegensatz zu den älteren Formulierungen von Guldberg und Waage, bei denen bloss die wirksamen Mengen in Reaktionsäquivalenten in Rechnung gezogen worden waren. Die Entwickelung der Wissenschaft hat unserem Forscher hierin wesentlich recht gegeben, und die von van't Hoff selbst nach dem Vorgange Horstmanns durchgeführte Anwendung der Energetik auf dieses Problem hat der ursprünglichen auf der Molekularhypothese beruhenden Begründung die zur Zeit sicherste Stütze gewährt. . .

"In der Anwendung der Thermodynamik auf die chemischen Probleme bewährt er alsbald die Meisterhand. Als Zeichen für die Weite seines Blickes und seine Fähigkeit, das Wesentliche in der Fülle der Erscheinungen zu sehen, sollen nur die Formulierung der Beziehung zwischen chemischem Gleichgewicht und elektromotorischer Kraft, sowie sein berühmtes Prinzip des beweglichen Gleichgewichts genannt werden, welches die Beziehung zwischen der Aenderung der Bedingungen eines Gebildes und der Beschaffenheit der Vorgänge ausspricht, die durch diese Aenderungen im Gebilde hervorgerufen werden.

"Die Wirkung des Buches war eine ähnliche, wie die seiner stereochemischen Ansichten: sie erfolgte nicht schnell, war aber um so tiefgreifender. Immer wieder wird die Forschung auch noch heute auf die Gedanken zurückgelenkt, die sich dort entwickelt finden, und der Umfang des Einflusses, den es

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[1] Z. physik. Chem., **31,** xiii (1899).

auf die Zeit und Arbeitsgenossen geübt hat, lässt sich auch nicht annähernd abschätzen."

This brings us to the third great epoch-making contribution of van't Hoff to chemistry in particular, and science in general; the relation between solution and gases, which is regarded by many physical chemists as his most important work. It is interesting to learn how van't Hoff came upon this problem, and especially interesting to learn it in his own language. In his celebrated Berlin lecture of 1894 before the German Chemical Society, and which led directly to his call to the University of Berlin, he tells the story.[1]

"Jung wie ich war, wollte ich dann auch die Beziehungen zwischen Constitution und chemischen Eigenschaften kennen lernen. Die Constitutionsformel soll ja doch schliesslich Ausdruck des ganzen chemischen Verhaltens sein.

"So entstanden meine 'Ansichten über die organische Chemie,' die Sie wohl nicht kennen. Es lohnt sich auch kaum. Nur hatten sie für mich den Werth, dass sie eine bestehende Lücke mir sehr scharf zeigten.

"Nehmen wir ein Beispiel!

"Wie bekannt, übt in organischen Verbindungen der Sauerstoff eine beschleunigende Wirkung auf fast sämmtliche Umwandlungen aus: Oxydation bei CH_4 schwerer als bei CH_3OH u. s. w.

"Um jedoch daraus werthvolle Beziehungen zu erhalten, ist genaue Kenntniss der Reactionsgeschwindigkeit Bedürfniss, und so gings zur Reactionsgeschwindigkeit, und es entstanden meine:

Etudes de dynamique chimique.

"Reactionsgeschwindigkeit zunächst als Hauptzweck. Chemisches Gleichgewicht aber unmittelbar daneben. Wo doch das Gleichgewicht einerseits auf Gleichheit zweier entgegengesetzter Reactionen beruht, und andererseits durch seine Verknüpfung mit der Thermodynamik eine feste Stütze gewährt.

"Sie sehen, um mein Ziel zu erreichen, kam ich stets weiter vom Ziel; das kommt öfter vor.

"Und weiter musste ich noch, denn die Gleichgewichtsfrage grenzt unmittelbar an das Affinitätsproblem, und so war ich angelangt bei der sehr einfachen Affinitätserscheinung, zunächst derjenigen, welche als Wasseranziehung sich äussert.

"Schon Mitscherlich hatte sich in seinem Lehrbuch der Chemie[2] die Frage gestellt nach der Grösse der Anziehung,

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[1] Ber. d. chem. Ges., **27**, 7 (1899).

[2] 4. Auflage, 565 (1844).

welche das Krystallwasser im Glaubersalz zurückhält. Ein Maass dafür erblickte er in der verminderten Krystallwassertension:

"'Wenn man in die Barometerleere bei 9° Glaubersalz bringt, sinkt das Quecksilber um 2.5 Linien (5.45 mm.) durch Wasserdampfabgabe. Wasser selbst bewirkt dagegen eine Senkung von 4 Linien (8.72 mm.)—die Affinität des Natriumsulfats zu seinem Krystallwasser entspricht also der Differenz 1.5 Linien (3.27 mm.) d. i. etwa 1/16 Pfd. (1/32 kg.) pro Quadratzoll (2.615 qcm.).'

"Dieser Werth, 1/200 Atm., kam mir unerhört klein, hatte ich doch den Eindruck, dass auch die schwächsten chemischen Kräfte sehr gross sind, wie es mir z. B. auch aus Helmholtz' Faraday Lecture hervorzugehen schien.

"So lag die Frage nahe, ob nicht noch in einfacheren Fällen diese Wasseranziehung in mehr directer Weise zu messen sei, und dann ist wohl die wässrige Lösung die einfachst denkbare, bedeutend einfacher als die Krystallwasserbindung.

"Mit dieser Frage auf den Lippen aus dem Laboratorium kommend, begegnete ich dann meinem Collegen de Vries und seiner Frau; der war gerade mit osmotischen Versuchen beschäftigt und machte mich mit Pfeffer's Bestimmungen bekannt."

This was the introduction of van't Hoff to the osmotic work of Pfeffer, and we all know more or less of the result. With that insight into the real meaning of phenomena, and that foresight that enables one to see relations from very meager and imperfect data, which are characteristic of the highest genius, van't Hoff saw from the few osmotic pressure measurements of Pfeffer the relations between solutions and gases—the laws of gas pressure applied to the osmotic pressure of solutions. In a word, we could deal with solutions as with gases.

The importance of this relation is obvious to any one. We know comparatively little of matter in the solid state, very little more than the forms in which it crystallizes, and the way in which it conducts certain forms of energy. We know more of matter in the liquid state, but even here our knowledge is far from satisfactory. When, on the other hand, we come to gases our knowledge is much more satisfactory. We know a great deal about matter in this most dilute condition, and can deal with gases satisfactorily from the thermodynamic standpoint.

When van't Hoff showed that we can deal with solutions by the same rigid methods that we employ with gases, he made a contribution not only to chemistry, but to science in general, the importance of which it is difficult to overestimate. A moment's thought will show how this is true. The whole subject of chemistry is primarily a science of solutions in the broader sense of that term. The same applies to geology, by solutions being meant not only solutions in water but in molten magmas as well. The subject of solutions is fundamental to practically every one of the biological sciences, experimental morphology, experimental botany, physiology, pharmacology, physiological chemistry, pathology, bacteriology, etc., and solutions play an important rôle in many branches of physics, especially in connection with the action of the primary cell.

It is obvious that any suggestion which would place the subject of solutions upon a scientific basis, and especially upon an exact basis, would be of fundamental importance not only for chemistry, but for all the natural sciences, and such was the relation between solutions and gases pointed out by van't Hoff.

van't Hoff not only showed the applicability of the gas laws to the osmotic pressure of solutions of nonelectrolytes, but he saw clearly the exceptions to these relations presented by electrolytes. In his great paper in the first volume of the *Zeitschrift für physikalische Chemie*, in which the above relations were formulated, he pointed out with equal clearness the exceptions presented by electrolytes—exceptions which a little later, in the hands of Arrhenius, led to the theory of electrolytic dissociation, another cornerstone in the structure of chemical science.

This was the third great contribution of van't Hoff to science, and from its wide-reaching significance is, in the opinion of the writer, the most important of them all.

We speak of van't Hoff having made three great contributions to chemistry in particular and to science in general. This is only by comparison. He opened up other fields which are only less important than the three in question and which would have made any less prominent man famous.

Take, for example, his paper on "Feste Lösungen."[1] Before this paper appeared we either never heard of the subject of solid solutions, or heard of it in a very casual way. In this paper van't Hoff pointed out that certain mixtures of solids have all the properties characteristic of solutions of solids or liquids in liquids—have all the properties of solutions in liquids as the solvent. Since the appearance of this paper, we have dealt with solid solutions as distinctively and almost as concretely as with liquid solutions; and in the hands of Ciamician and his coworkers, and of Küster, important developments have resulted.

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[1] Z. physik. Chem., **5**, 322 (1890).

The most recent experimental work of van't Hoff in connection with the tremendously complex problems presented by the various salt beds deposited from desiccated inland seas, has geological interest: but this work is not in the same class with that discussed above.

This sketch of the work of van't Hoff would be unnecessarily imperfect and unsatisfactory were not something said in reference to the personality of this great man.

The writer had the good fortune to know van't Hoff in the relation of student to teacher for a short time in the spring of 1894.

My chief object in going to his laboratory was to learn, if possible, the methods by which he worked. When dealing with any problem, he would collect all of the reasonably reliable data bearing upon that problem, bring it together and study it.

The question has often come up whether van't Hoff was a great experimenter. This is a matter of very little consequence. He did not need to experiment. There are plenty of others to do that. He was primarily an interpreter of the experimental results obtained by others, and he interpreted these results in such a way as to revolutionize chemistry.

During the short period that I was in his laboratory in Amsterdam, he worked continually and very intensely in his laboratory, but the results of that work were never published, and this is the key to the difference of opinion that prevails in reference to van't Hoff the experimenter. He did not publish the results that he obtained simply for their own sake. If they bore on some theory or generalization in which he was interested they were published. If not, or if their meaning was not clear, they never saw the light. He seemed to look upon his own experimental work as valuable, not in itself, but only as it proved or disproved some idea that he had in mind. Consequently, a large amount of the work that he did in the laboratory with his own hands was never published.

During the Amsterdam period van't Hoff impressed me as one who was living under an intense nervous and mental strain. His walk, his speech, and the characteristic nervous twitch of the eye all pointed in this direction. For power of concentration and intensity, I know of only one other who could be compared with him, and that was Rowland.

After going to Berlin van't Hoff seemed to have lost some of his earlier intensity, probably due to the progress of the horrible malady which brought such an untimely end.

When I saw him last, a year and a half ago, although he was suffering very severely, the same personal characteristics that marked his earlier life were still there. An unusual modesty, a dislike for all show and ostentation, a simple, frank, open, honest, unselfish nature were a few of the attributes that must have impressed themselves upon all who knew him.

van't Hoff enjoyed what is not given to all great men. He lived to see his work fully recognized and appreciated. He was elected a member of most of the learned societies and academies of the world, and was awarded the first Nobel prize in chemistry, which shows how he was valued by the leading chemists of his day.

Although it always requires time to fix the exact position of any great man, yet we are certainly justified in placing van't Hoff in the very first rank of such men as Dalton, who gave us the laws of definite and multiple proportions; Avogadro, whose hypothesis has done so much for chemistry; Berzelius, the father of analytical chemistry; Lavoisier, who told us what combustion really is; Liebig, who transplanted chemistry from France to Germany; Wöhler, who coöperated with Liebig in his most important work; Kekulé, who gave a new impulse to organic chemistry; Hofmann, Baeyer and Victor Meyer, who took up organic chemistry where Liebig, Wöhler and Kekulé left it, and showed us its real meaning for science as well as for the material good of the human race; Fischer, who, influenced by the stereochemical conceptions of van't Hoff, made organic chemistry what it is to-day; Ramsay, who not only discovered the rare gases in the atmosphere and in the earth, but who showed us the birth of a new element; Arrhenius, who has furnished chemistry with one of the greatest generalizations of all times; Ostwald, who contributed so much experimentally to the development of modern physical chemistry, and who brought order and system into the entire science of physical chemistry, not to say of chemistry in general.

Without presuming to compare van't Hoff with these other great men, his work stands out not simply for the *importance* of the generalizations which he reached, but for their *number*.

The question that men of science will ask is, When shall we have his like again?

HARRY C. JONES.

LEONARD PARKER KINNICUTT.

The death of Prof. Leonard Parker Kinnicutt, well known through his contributions to sanitary chemistry and a recognized expert on sewage disposal and water supply, was announced February 6th. Prof. Kinnicutt was born at Worcester, Mass., May 22nd, 1854. His early training was received at the Massachusetts Institute of Technology, where he obtained the degree of B.S. in 1875. He studied four years at Heidelberg and Bonn and one year at the Johns Hopkins University, and in 1882 made his D.Sc. at Harvard, where he had been instructor in quantitative analysis since 1880. The following year he was appointed assistant professor of chemistry at the Worcester Polytechnic Institute and remained at that institution till the day of his death, being promoted to a full professorship in 1886 and made director of his department in 1892. He took an active interest in questions of public health and for the last eight years served as consulting chemist to the Connecticut Sewerage Commission. He was a member of many scientific societies. His main contributions to science and the public welfare have dealt with sewage disposal; sanitary problems in connection with air and water; quantitative methods of determining carbon monoxide; standard methods in the analysis of potable waters and sewage; septic tank and intermittent filtration methods for the treatment of sewage.

REVIEWS.

A TEXT BOOK OF ORGANIC CHEMISTRY. BY WILLIAM A. NOYES, Professor of Chemistry in the University of Illinois. Second edition, revised. New York: Henry Holt and Company. 1910. pp. xvii + 537.

In regard to this edition the author says, "The chapter on Compounds of Interest in Physiology and Pathology has been rewritten on the basis of the classification of proteins recently adopted by the American Society of Biological Chemists and the American Physiological Society." He further says: "A number of other changes and additions, most of which were prepared for the German edition of this book, have also been included." When the first edition appeared the book was noticed in THIS JOURNAL[1] and reference may here be made to what was then written in regard to it. The fact that a second edition is called for is further evidence that the author's method of presentation has found favor with a fair number of scholars. It is further interesting to note that the book has been translated into German and that no less a chemical light than Ostwald has written an Introduction to the German edition. The author is to be congratulated upon the success of his book.

[1] THIS JOURNAL, **31**, 85.

GRUNDLAGEN UND ERGEBNISSE DER PFLANZENCHEMIE. Nach der schwedischen Ausgabe bearbeitet von H. EULER, Professor der Chemie an der Universität Stockholm. Zweiter Teil: Die allgemeinen Gesetze des Pflanzenlebens. Dritter Teil: Die chemischen Vorgänge im Pflanzenkörper. Braunschweig: Friedrich Vieweg und Sohn. 1909. s. viii + 298. Prices, geh., M. 7; geb., M. 8.

This volume, which embodies the second and third parts of the work on "Pflanzenchemie" now completed by our brilliant and versatile colleague, is even more attractive than the first one.

In a very entertaining introduction Euler shows the debt which botanists, especially the newer school of plant physiologists, owe to organic and physical chemistry.

In the second part he takes up the general laws of plant life and discusses in detail, with full references, the importance to the plant chemist of osmotic pressure, the mass law, electrolytic dissociation, solubility, colloids, reaction velocities, the plant enzymes (including hydrolytic enzymes, fermentative enzymes, oxidases and catalases), the influence of temperature and light on chemical reactions, and optical activity.

In the third part the chemical processes of the plant life are discussed in the sections on the assimilation of carbon, nitrogen, and minerals, and on respiration, fermentation, and the synthesis of proteids, carbohydrates, and fats. The end products of the synthetic processes and their relation to plant growth and the development of the individual organs are fully treated. There is finally an interesting chapter on the origin of organic compounds, life phenomena, and organized entities.

All chemists and botanists will find much pleasant and instructive reading in this book. S. F. ACREE.

ANALYTICAL CHEMISTRY. Volume II. Quantitative Analysis. BY F. P. TREADWELL, PhD., Professor of Chemistry in the Polytechnic Institute of Zurich. Authorized Translation from the German by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Second Edition. Thoroughly revised and enlarged. New York: John Wiley & Sons. London: Chapman and Hall, Limited. 1910. pp. x + 787.

The number of authoritative works dealing with general analytical procedures, and of such scope as to be useful alike for practitioner and student, is not large to-day and it is fortunate that the author and translator of this well-recognized hand-book are so painstaking in its revision. The present edition merits the same favorable comments as its predecessor. This, the second edition, is translated from the fourth German edition, and the translator has added a number of procedures which have found favor among American chemists, but have not as yet been incorporated in the German edition. Among the latter are Blasdale's separation of calcium and magnesium, the determination of nickel as glyoxime, and that of zinc as zinc ammonium phosphate, the determination of nickel in steel (Brünck), a procedure for the analysis of bronzes, the determination of vanadium, molybdenum, chromium, and nickel in steel, the Bamber method for sulphur in iron or steel, some modifications of the procedure for carbon in steels, the Brown method for silicon, the bismuthate and Williams method for manganese, the Blair rapid method for phosphorus, the iodate method for copper, the cyanide titration for nickel, the Low method for copper, and the use of rotating electrodes for a number of determinations. The procedures thus added are generally recognized as useful and reliable, and the details as given are, in nearly all cases, those found desirable by the translator on the basis of his instructional experience and private analytical practice. The volume can be heartily commended to the attention of all analysts and teachers. H. P TALBOT.

A COURSE OF QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES, with Explanatory Notes. BY OLIN FREEMAN TOWER, Ph.D., Hurlburt Professor of Chemistry in Adelbert College of Western Reserve University. Philadelphia. P. Blakiston's Sons & Co. 1909. pp. xi + 83.

Professor Tower's book is written from a physical-chemical standpoint; its great advantage is its conciseness and clearness. The introduction is only 14 pages in length, but it is an admirably clear explanation of the application of modern ideas to analysis. Few equations are given and there are no tables. The author employs the method of Noyes and Bray for separating antimony from tin, the basic acetate method for the iron group, and separates strontium from calcium by amyl alcohol.

In the reviewer's opinion this is one of our best laboratory manuals for college work. E. R.

QUALITATIVE CHEMICAL ANALYSIS FROM THE STANDPOINT OF SOLUBILITIES, IONIZATION AND MASS ACTIONS. BY J. I. D. HINDS, Ph.D., LL.D., Professor of Chemistry, University of Nashville and Peabody College for Teachers, Nashville, Tennessee. Easton, Pa.: Chemical Publishing Company. 1910. pp. vii + 266. Price, $2.00.

The ground covered in this book is the same as in the average college manual. The theoretical part is clear, the older standard methods are generally retained, but the author introduces the Benedict method for the separation of cobalt and nickel. The properties and reactions of the elements are given with unusual fullness. Fifty pages are given to principles and methods and over 200 pages to properties, reactions and analysis.

The great length of the book compared with the ground covered, the printing of all the equations in full instead of allowing the student to work them out for himself, and the use of tables may all be criticized. The book is carefully compiled however, and merits examination. E. R.

TRAITÉ COMPLET D'ANALYSE CHIMIQUE APPLIQUÉE AUX ESSAIS INDUSTRIELS. PAR J. POST, Professeur Honoraire à l'Université de Goettingue, et B. NEUMANN, Professor à la Technische Hochschule de Darmstadt. Avec la collaboration de nombreux chimistes et spécialistes. Deuxième édition française traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. CHENU, Ing. E. P. C., et M. PELLET, Ing. I. N. A. Tome second. Troisième fascicule. Paris: Librarie scientifique A. Hermann et Fils. 1910. pp. 418. Price, Fr. 13.

This portion of Post's Technical Analysis comprises the examination of beer, wine, cider and perry, alcohol, compressed yeast, vinegar and wood alcohol. The methods given are for the most part the customary ones established by general usage. The results of the latest researches are not always incorporated and the reader will look in vain for several processes which have been shown by recent work to possess distinct advantages over those formerly in use. Conservatism in this respect, however, is hardly to be regarded as a defect in a book intended as a standard work in a broad field. Much space is devoted to the official German and French methods. As a compilation of standard methods of these countries the book is distinctly useful. A. G. WOODMAN.

ENGINEERING CHEMISTRY. A Manual of Quantitative Analysis for the Use of Students, Chemists and Engineers. BY THOMAS B. STILLMAN, M.Sc., Ph.D., Late Professor of Engineering Chemistry in the Stevens Institute of Technology. With 174 Illustrations. Fourth edition. Easton, Pa.: Chemical Publishing Co. 1910. pp. ix + 744. Price, $5.

The fourth edition of this widely used work contains all the valuable features of its predecessors, with considerable amplification of some of the sections. Most notable of these additions occur in the chapters on Fuels, Boiler Waters, Pyrometry, Lubricating Oils, and Paints. The contributed articles on Foundry Chemistry, Official Methods of Sampling Iron Ores, and Acetylene are new.

As a whole, this treatise fills a well-defined need of the practical chemist and engineer; in the principal branches of technology it furnishes methods for the analysis of raw materials and products, in some cases notes on the processes themselves and on control of the same, and in many others methods of physical testing and good recent specifications for the guidance of manufacturers and buyers. The best of these are probably the sections on Fuels, Water, Portland Cement, Paper, Soap, and Lubricating Oils. In addition there are numerous valuable tables, while throughout the book are given copious references to original sources and to extended treatments of the various subjects. As a ready, suggestive reference book it is therefore warmly commended to practitioners and students. There are, however, features open to criticism.

The arrangement and distribution of space are poor. The chapter on Alloys is desultory, and comes between those on Paper and Gelatin Dynamite, while Pyrometry is treated near the end of the book. There are thirteen pages devoted to the causes of saline efflorescence in bricks, but only two to the technology of rubber. Seven viscosimeters are described and illustrated, while only the Berthelot type of calorimeter is treated. This haphazard method extends alike to the internal material of the various chapters. Portland cement receives good treatment from many angles, while steel is dismissed with short methods for chemical analysis, some unreliable remarks on its microstructure, and a general classification of its grades. There are too many pages of unedited contributions and not enough of well-digested authoritative matter.

The methods for analysis given are generally of the rough and ready type, giving quick results, of doubtful accuracy. Realizing the technical demand for speed, we would not eliminate these methods entirely, but suggest the insertion of alternate procedures for the benefit of those desiring a higher degree of accuracy. Careful editing and revision would double the value of this work, which now impresses the reader as a voluminous note book.

K. W. ZIMMERSCHIED.

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CHEMICAL JOURNAL

THE ACTION OF LIGHT ON ESTERS OF α-CYANCINNAMYLIDENACETIC ACID.

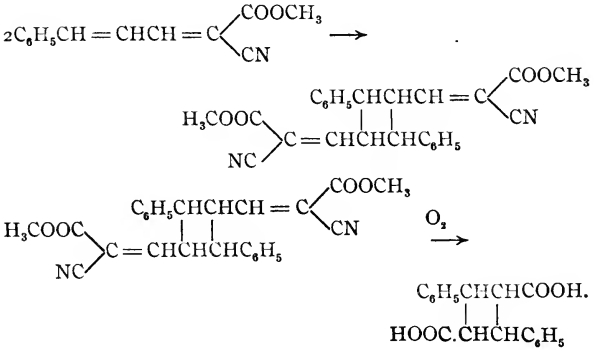
BY MARIE REIMER.

While carrying out reactions between cinnamylidene esters and Grignard's reagent, it was noticed that these esters are very sensitive to light. A bottle containing crystals of ethyl α-phenylcinnamylidenacetate, for example, which had been standing on a laboratory shelf for several months, was found to be coated with a pasty product smelling strongly of benzaldehyde. A sample of ethyl cinnamylidenacetate which had been standing a year was found to have changed entirely to a pasty substance which smelled of benzaldehyde. In the case of ethyl α-methylcinnamylidenacetate this decomposition is so rapid that the ester must be kept carefully protected from the light and purified immediately before it is used. Esters of cinnamylidenemalonic acid change more slowly, a decolorization taking place at the same time. With esters of α-cyancinnamylidenacetic acid this decolorization is the main reaction, little or no pasty product being formed. All of these changes are more rapid in direct sunlight.

In view of the important results obtained by the study of the action of light on organic compounds, it seemed of interest to investigate this reaction on a series of these esters. These experiments are now being carried on in this laboratory. The present paper deals only with results obtained in the study of the action of light on esters of α-cyancinnamylidenacetic acid which was chosen as the member of the series having the most negative group in the α-position.

The reaction of light on a few cinnamylidene compounds has been investigated. Cinnamylidenemalonic acid loses color rapidly in the sunlight with the formation of a tetramethylene derivative,[1] a reaction analogous to that of cinnamic acid under the same conditions.[2] α-Methylcinnamylidenacetic acid also polymerizes to form a colorless tetramethylene compound[3] similar in structure to that obtained from the malonic acid.

For the study of this reaction on esters of α-cyancinnamylidenacetic acid the methyl and ethyl esters were chosen. The reaction of the methyl ester in the sunlight has been found to be exactly analogous to that of the cinnamylidene acids previously investigated. The colorless product obtained by exposure of this compound is dimethyl diphenyltetramethylenebismethylenecyanacetate, the structure being proved by the fact that the product of oxidation is α-truxillic acid:



$$2C_6H_5CH=CHCH=C\left\langle\begin{matrix}COOCH_3\\ CN\end{matrix}\right. \longrightarrow$$

$$\begin{matrix} & & C_6H_5CHCHCH=C\left\langle\begin{matrix}COOCH_3\\ CN\end{matrix}\right. \\ \begin{matrix}H_3COOC\\ NC\end{matrix}\right\rangle & C= & CHCHCHC_6H_5 & \end{matrix} \xrightarrow{O_2}$$

$$\begin{matrix} C_6H_5CHCHCOOH. \\ | \quad | \\ HOOC.CHCHC_6H_5 \end{matrix}$$

The behavior of the ethyl ester on exposure is, unexpectedly, quite different from that of the methyl compound. The first reaction is one of decomposition. The mass becomes

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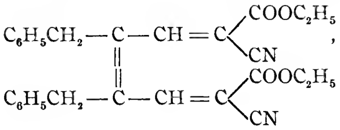
[1] Riiber: Ber. d. chem. Ges., **35**, 2411.

[2] Riiber; *Ibid.*, **35**, 2908.

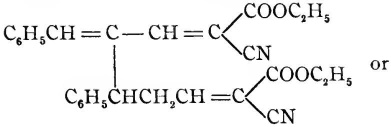
[3] Macleod: THIS JOURNAL, **44**, 331.

slightly sticky and smells of benzaldehyde. This reaction is accompanied by a decolorization, the speed of which is greater than that of the decomposition, as the quantity of pasty product does not increase appreciably after 8–10 hours, while the yellow color of the ester gradually disappears. After exposure, the colorless product, separated from oil and unchanged ester, was found to be a dimeric form of the original substance. It has not, however, the same structure as the compound obtained from the methyl ester. On oxidation it gives benzaldehyde and no trace of any truxillic acid, showing that the group $C_6H_5CH=$ is present and that there is no tetramethylene ring. For the structure of such a compound there are a number of possibilities. It is scarcely to be expected that an addition of the molecules would take place at the 1,2 double linkage because of the negative character of the groups attached to the α-carbon atom. If the addition is at the 3,4 double linkage, in order that one $C_6H_5CH=$ group be present in the dimolecular product there can be but a single carbon linkage between the molecules. Such a formula as



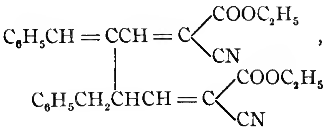
$$\begin{array}{l} C_6H_5CH_2-C-CH=C{<}^{COOC_2H_5}_{CN}, \\ \qquad\qquad\quad\;\, \| \\ C_6H_5CH_2-C-CH=C{<}^{COOC_2H_5}_{CN} \end{array}$$

for example, could not be possible. Formulas which more nearly express the reactions of the compound are



$$\begin{array}{l} C_6H_5CH=C-CH=C{<}^{COOC_2H_5}_{CN} \\ \qquad\qquad\;\; | \\ \qquad C_6H_5CHCH_2CH=C{<}^{COOC_2H_5}_{CN} \end{array} \quad \text{or}$$

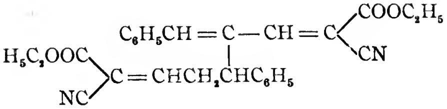
I.



$$\begin{array}{l} C_6H_5CH=CCH=C{<}^{COOC_2H_5}_{CN}, \\ \qquad\qquad\quad\;\; | \\ \quad C_6H_5CH_2CHCH=C{<}^{COOC_2H_5}_{CN} \end{array}$$

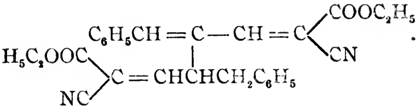
II.

or a more stable configuration might be



or

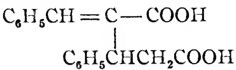
I*a*.



II*a*.

A closing of a ring through nitrogen is also not impossible, though none of the reactions of the compound point to such a structure.

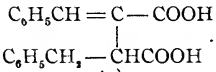
Results obtained by oxidation of this polymeric compound make probable the structures I or II, but do not make it possible to decide between them. The reaction of bromine on the esters, however, points strongly to formula I and to the configuration expressed by I*a*. Results are as follows: Oxidation of the polymeric ester with potassium dichromate gives as product an acid with the composition of a truxillic acid which contains, however, the group $C_6H_5CH=$, as it immediately decolorizes an alkaline solution of permanganate in a freezing mixture with formation of benzaldehyde. For such a compound there are possible the formulas



$$\begin{array}{l} C_6H_5CH=C-COOH \\ \qquad\qquad\;\, | \\ \quad C_6H_5CHCH_2COOH \end{array}$$

(1)

or

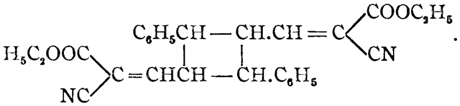


$$\begin{array}{l} C_6H_5CH=C-COOH \\ \qquad\qquad\quad\;\, | \\ C_6H_5CH_2-CHCOOH \end{array}$$

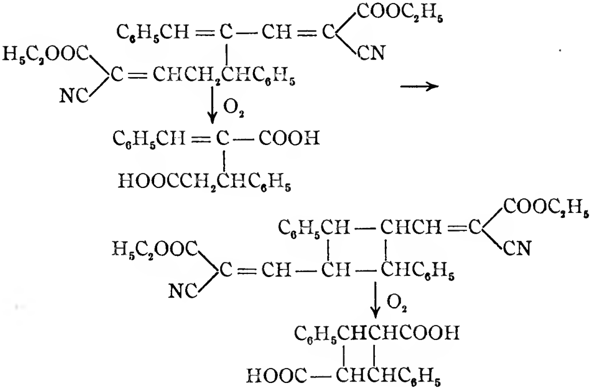
(2)

Oxidation of esters (I) and (II), respectively, would yield compounds having such constitution. Potassium permanganate oxidizes the substance to benzoic acid and an acid of the composition $C_{11}H_{10}O_5$, which might be obtained from (1) or (2). It has not, as yet, been possible to determine the structure of this compound.

By the action of bromine on a solution of the polymeric ester, which melts at 166°, this ester was transformed into an isomer melting at 128°. This latter compound is exactly analogous in behavior to that obtained by the action of light on methyl α-cyancinnamylidenacetate. It has been proved to be ethyl diphenyltetramethylenebismethylenecyanacetate,



The formation of this compound from the higher melting polymeric ester makes most probable formula (I) advanced for that ester and, preferably, the configuration (I*a*). Isomerization of this compound to a tetramethylene derivative would involve the shifting of one hydrogen atom and closing of the tetramethylene ring. From a compound of formula (II), on the other hand, such a transformation would necessitate the breaking of a bond between carbon atoms and the subsequent closing of the tetramethylene ring. Formula (I*a*) is therefore to be preferred for the polymeric ethyl ester formed by exposure of the monomolecular ester to the light and, consequently, formula (1) for the acid obtained by oxidation of this ester:



It seemed scarcely probable that the difference in the reaction of methyl and ethyl α-cyancinnamylidenacetates in the light was due to the different chemical effect in the molecule of the methyl and ethyl groups. A more plausible explanation would seem to be that the two esters differ in configuration, one form being more stable for the methyl, the other for the ethyl ester. By the usual methods of preparation, only one form of each ester was obtained. Attempts to prepare a second ethyl ester from the methyl compound were, however, successful. Unstable ethyl α-cyancinnamylidenacetate was prepared by the action of potassium ethylate on the methyl ester in absolute ethyl alcohol solution.[1] This compound has, without doubt, the same configuration as the methyl ester from which it was formed, as its behavior is exactly analogous. On exposure to the light it loses color rapidly. The colorless product is diethyl diphenyltetramethylenebismethylenecyanacetate, melting at 128°, identical with the compound formed by isomerization, under the influence of bromine, of the high-melting dimeric ethyl ester. This new ethyl ester is unstable and changes over into the stable form on melting.

The transformations of these esters are, therefore, as shown in the scheme on the opposite page.

EXPERIMENTAL.

Action of Light on Methyl α-Cyancinnamylidenacetate.—α-Cyancinnamylidenacetic acid was prepared by a modification of the method of Fiquet.[2] One hundred grams of sodium cyanacetate and 125 grams of cinnamic aldehyde were heated for 45 minutes to a temperature of 180°. The reaction product was dissolved in the smallest possible quantity of boiling water, from which, on cooling, the sodium salt of α-cyancinnamylidenacetic acid separated in bright yellow, glistening plates. The acid obtained from this salt was pure after one crystallization from alcohol. The methyl ester was prepared by the method of Fiquet.[3] The ester may be prepared even

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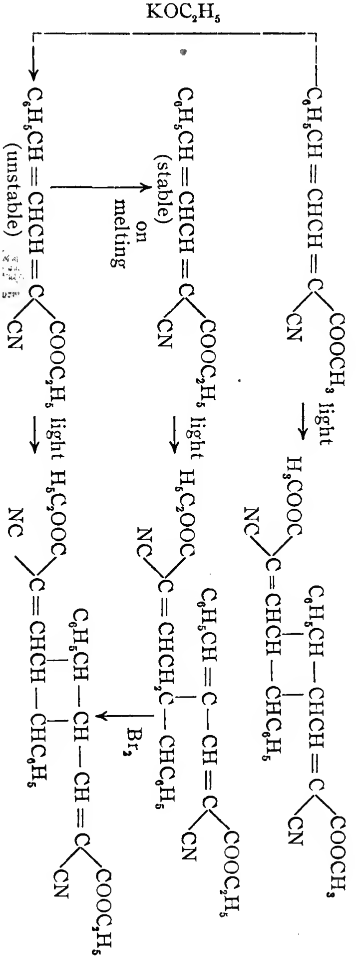
[1] Cf. Pfannl: Monats. Chem., **31**, 301.

[2] Ann. Chim. Phys., [6] **29**, 492.

[3] *Loc. cit.*


KOC₂H₅
(unstable)
(stable)
on melting
light
light
light
Br₂

more readily by condensation of methyl cyanacetate with cinnamic aldehyde in the presence of sodium methylate according to the directions of Bechert[1] for the ethyl ester. The ester, after several recrystallizations from methyl alcohol, melts sharply at 145°.

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent.	Gram substance.	Rise in boiling point.	Molecular weight.
48.95	0.5693	0.142	215
48.95	0.9184	0.226	217
	Calculated for $C_{13}H_{11}O_2N$,		213

In diffused daylight the ester loses its yellow color slowly. In the sunlight it crumbles rapidly to a white powder. In order to obtain this colorless product in quantity, the ester was finely powdered, spread out in a thin layer on plates of glass and exposed to the direct sunlight. As it was not possible in this way to determine the speed of reaction compared with that of other cinnamylidene esters because of the varying intensity of the sunlight, a mercury-vapor lamp was used for this purpose. Ten grams of ester were spread out as evenly as possible over glass plates twelve inches square and placed at an average distance of 24 cm. from the source of light. This was a Cooper Hewitt lamp of the tubular type, 67.5 cm. long, carrying a current of 3.2 amperes. The whole was protected from the sunlight by a covering of black cloth lined with white. The ester was stirred and spread out again every four hours. The temperature was 35° during exposure. In later experiments a tube of uviol glass was used, but the speed of reaction was not appreciably increased.

After exposure for 30 hours, 94 per cent. of the ester was found to have been decolorized. The product was washed thoroughly with ether and then with cold alcohol to rid it of small quantities of unchanged yellow ester. Even after much longer exposure there was always a trace of yellow ester left, probably because it had been protected from the light by the colorless product. The latter was purified by dissolving it in the smallest possible quantity of boiling ace-

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[1] J. prakt. Chem., [2] 50, 14.

tone and adding an equal volume of low-boiling ligroin. It separates in clumps of hard, clear crystals, melting at 172°.5. The compound is readily soluble in benzene chloroform and acetone; very slightly soluble in hot ether and alcohol; insoluble in ligroin.

Analysis:

0.1847 gram substance gave 0.4982 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_{26}H_{22}O_4N_2$.	Found.
C	73.24	73.56
H	5.16	5.20

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent.	Gram substance.	Rise in boiling point.	Molecular weight.
51.06	0.6703	0°.038	426
51.06	0.9040	0°.107	431
		Calculated for $C_{26}H_{22}O_4N_2$,	426

The compound is, therefore, a dimeric form of the original ester.

The structure of this compound was determined by oxidation. Ten grams were dissolved in one liter of acetone and finely powdered potassium permanganate added slowly as long as decolorization took place. The solution was cooled by running water during oxidation. As soon as the permanganate was no longer decolorized rapidly the excess was decomposed by sulphur dioxide and the solution filtered. The oxides of manganese were washed with acetone and then extracted repeatedly with hot water. The aqueous solution deposited, when acidified, an acid which was purified by crystallization from methyl alcohol. It separated in clear prisms, which rapidly became opaque on exposure to the air and melted at 274°.

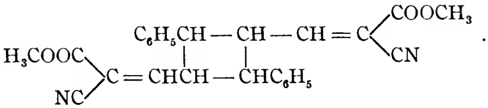
Analysis:

0.1765 gram substance gave 0.4741 gram CO_2 and 0.090 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found.
C	72.97	73.25
H	5.40	5.69

The analysis and properties point to α-truxillic acid. That it was α-truxillic acid was shown by melting it with a sample of that acid obtained from another source. The mixture melted sharply at 274°. From the aqueous filtrate were obtained benzoic and oxalic acids.

The formation of these products on oxidation shows the dimeric ester to be dimethyl diphenyl-α-cyancinnamylidenacetate,



$$\begin{array}{l} \qquad\qquad\qquad\; C_6H_5CH - CH - CH = C{\begin{array}{l} COOCH_3 \\ CN \end{array}} . \\ {\begin{array}{l} H_3COOC \\ NC \end{array}}\!\!>\! C = CHCH - CHC_6H_5 \end{array}$$

The solution of the compound in concentrated sulphuric acid has a bright lemon-yellow color. When this solution is poured into water the colorless compound is precipitated unchanged. When distilled, under 20 mm. pressure, the ester is depolymerized. The distillate solidifies in the receiver and, after one crystallization, melts sharply at 145°. This is analogous to the behavior of the polymeric products obtained by exposure of cinnamylidenmalonic and -methylacetic acids.

All attempts to saponify the ester in order to gain the corresponding tetramethylene acid gave only the monomolecular α-cyancinnamylidenacetic acid. This tetramethylene ring is, therefore, more easily broken down than that in the ester of diphenyltetramethylenebismethylenepropionic acid,[1] as the latter is saponified to the corresponding dimeric acid by boiling with aqueous potash.

Bromine reacts on the compound only to a very slight degree. Five grams of ester were dissolved in chloroform, 3.7 grams (1 mol.) of bromine added and the solution allowed to stand at 0° for two weeks. After this length of time there was no apparent change in the color of the solution. The solvent was allowed to evaporate spontaneously. The white crystalline product which separated was shown to be unchanged ester. Over 80 per cent. was regained. A very

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[1] Macleod: *Loc. cit.*

small quantity of a volatile bromine compound was also formed, but not in sufficient quantity for investigation. This was probably formed by substitution. These results were to be expected from a compound of the structure of this ester, as the negative groups attached to the α-carbon atom would interfere with the addition of bromine to the α,β double linkage.

Action of Light on Ethyl α-Cyancinnamylidenacetate.—The ethyl ester was prepared by the method of Bechert.[1]

Molecular weight determined in boiling benzene ($K = 26.1$):

Grams solvent.	Grams substance.	Rise in boiling point.	Molecular weight.
48.51	0.3064	0°.073	228
48.51	1.0167	0°.247	221
		Calculated for $C_{14}H_{13}O_2N$,	227

On exposure to the light the ester became a little pasty and the odor of benzaldehyde was evident. The color disappeared but slowly. Under exactly the same conditions of exposure as were used for the methyl ester, a 53 per cent. yield of colorless product was obtained after 60 hours. The amount of decomposition product was small, but evidently sufficient to protect much of the ester from the action of the light so that no amount of stirring was sufficient to expose all parts. As the decomposition reaction is evidently analogous to that of other cinnamylidene esters under investigation in which much larger amounts of pasty products are formed, the study of the small quantity obtained from the ester under consideration has been deferred until these other products have been investigated.

The reaction product was treated with alcohol at 40° to separate the colorless compound from unchanged ester and oily products. The pure white powder left was crystallized from boiling alcohol. It separates in clumps of branching white crystals melting at 166°. It is readily soluble in chloroform, acetone and benzene; slightly soluble in alcohol, boiling ligroin and ether.

Analysis:

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[1] *Loc. cit.*

0.1749 gram substance gave 0.4729 gram CO_2 and 0.0949 gram H_2O.

	Calculated for $C_{28}H_{26}O_4N_2$.	Found.
C	74.00	73.74
H	5.72	6.02

Molecular weight determined in boiling benzene (K = 261):

Grams solvent.	Gram substance.	Rise in boiling point.	Molecular weight.
52.24	0.2936	0°.033	444
52.24	0.4286	0°.051	417
52.24	0.8970	0°.108	415
	Calculated for $C_{28}H_{26}O_4N_2$,		454

The compound is a dimeric form of ethyl cyancinnamylidenacetate. It is not, however, analogous to that obtained from the corresponding methyl ester. It is much less stable than the latter and its reactions show it to be structurally different.

The compound decomposes slowly on boiling with alcohol, the solution becoming yellow. It dissolves readily in concentrated sulphuric acid. This solution, of a brilliant crimson color, when poured into water deposits a bright yellow solid which is a mixture of products from which no pure substance has been obtained. A complicated decomposition takes place on saponification. When distilled under diminished pressure, the distillate was found to consist of a mixture of stable and unstable ethyl α-cyancinnamylidenacetates. It is probable that the first reaction is the rearrangement of the compound into its tetramethylene isomer, decomposition of this into the unstable ethyl ester, analogous to the behavior of the methyl compound, and change of part of the unstable to the stable ester.

Attempts to determine the structure of the compound by oxidation have, so far, been only partially successful. With a solution of potassium permanganate in the cold, benzaldehyde is formed. The compound contains, therefore, the group $C_6H_5CH=$. The final products of oxidation with permanganate were found to be benzoic acid and a trace of an acid melting at about 179°. The quantity of this acid obtained in repeated experiments was not enough for analysis. When potassium dichromate in glacial acetic acid was used for the oxidation there was obtained, beside benzoic acid, a trace of another acid melting at 185°. A good yield of this latter compound was obtained when the reaction was carried out in 50 per cent. acetic acid. Two grams of the ester were added to 100 cc. of 50 per cent. acetic acid in which 5 grams of potassium dichromate were dissolved. The mixture was boiled for about 15 minutes until the ester had gone into solution. From the reaction mixture the solvent was allowed to evaporate at room temperature for 48 hours. The liquid was then found to be filled with yellow plate-like crystals. These were washed with water and recrystallized from dilute methyl alcohol. The compound was found to be an acid which, after repeated crystallizations, separates in fine white needles melting at 185°. At 260° evolution of a gas begins.

Analysis:

0.1559 gram substance gave 0.4181 gram CO_2 and 0.0801 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found.
C	72.97	73.13
H	5.40	5.70

? see errata p. 634

The acid is readily soluble in acetone, chloroform and alcohol; sparingly soluble in ether and benzene; insoluble in water.

The *methyl ester* was prepared by dissolving 5 grams of the acid in 100 cc. of methyl alcohol saturated with hydrochloric acid. The mixture was shaken vigorously until the acid was all in solution. The methyl ester began to crystallize out of solution almost immediately. A quantitative yield was obtained. The compound is readily soluble in hot methyl and ethyl alcohols and ether, very sparingly soluble in these solvents in the cold. It separates from methyl alcohol solution in clear rhombic crystals melting at 132°.

Analysis:

0.1736 gram substance gave 0.4708 gram CO_2 and 0.0973 gram H_2O.

	Calculated for $C_{18}H_{14}O_4(CH_3)_2$.	Found.
C	74.07	73.98
H	6.17	6.22

These results show that the acid is dibasic and that the two carboxyl groups are not attached to the same carbon atom, as the acid does not begin to decompose until heated 75° above its melting point. As an alkaline solution immediately decolorizes potassium permanganate in a freezing mixture with formation of benzaldehyde, the group $C_6H_5CH=$ is present.

It was very difficult to obtain pure products by the oxidation of this acid. After repeated failures the experiment was carried out as follows: Four and five-tenths grams of acid were dissolved in acetone which was kept cold in a freezing mixture and 5.5 grams of potassium permanganate were added during the course of one hour. The excess of oxidizing agent was then decolorized with sulphur dioxide and the oxides of manganese filtered. The acetone was allowed to evaporate spontaneously from the filtrate. The oxides of manganese were dissolved with sulphur dioxide in dilute sulphuric acid and the solution extracted with ether. As the same products were obtained from the ether and acetone solutions and as they were not very soluble in ether, it was found best in subsequent experiments to make the acetone solution strongly acid with sulphur dioxide when the excess of permanganate was decolorized. After removal of the solvents by spontaneous evaporation, the residues were treated with hot water. The aqueous solution deposited, on cooling, a mass of fine white needles which were a mixture of benzoic acid and an acid melting at 179° with violent evolution of carbon dioxide. This mixture was carefully dried in the air and the acids separated by extraction with chloroform. From the chloroform solution a quantitative yield of benzoic acid was obtained. The residue, not soluble in chloroform, is an acid very soluble in ethyl and methyl alcohols, hot water and acetone, much less soluble in ligroin and ether. Repeated attempts to recrystallize the acid were unsuccessful. The only solvent from which it separates in a crystalline condition is hot water, which cannot be used successfully, however, as the acid loses carbon dioxide at the temperature at which solution takes place. This accounts for the small yield of this acid obtained—28 per cent. of the calculated on the basis of structure (1) or (2). The residue from the chloroform extraction, which melts sharply at 179°, was therefore used in subsequent work.

Analysis of air-dried acid:

0.1505 gram substance gave 0.2938 gram CO_2 and 0.0743 gram H_2O.

	Calculated for $C_{11}H_{10}O_5$.	Calculated for $C_{11}H_{10}O_5.1.5H_2O$.	Found.
C	59.49	53.01	53.84
H	4.50	5.22	5.48

The acid was then allowed to stand over sulphuric acid in a desiccator; sample I for twelve days, sample II for six weeks.

I. 0.1553 gram substance gave 0.3232 gram CO_2 and 0.0715 gram H_2O.

II. 0.1603 gram substance gave 0.3363 gram CO_2 and 0.0715 gram H_2O.

	Calculated for $C_{11}H_{10}O_5.0.5H_2O$.	Found.	
		I.	II.
C	57.10	56.76	57.21
H	4.70	5.11	4.95

The composition of the acid agrees with that of an acid, $C_{11}H_{10}O_5$, containing 0.5 molecule of water of crystallization. The acid was shown to contain water of crystallization in the following way: A small quantity of sample II was mixed with an equal bulk of anhydrous cupric sulphate and heated in an oil bath. At 179° the acid melted to a clear liquid. Carbon dioxide was given off and, at the same time, the cupric sulphate became a brilliant blue. It was not found possible to drive off this water of crystallization below the temperature at which the acid loses carbon dioxide. Neither has it as yet been possible to purify the substance formed by loss of carbon dioxide from the acid. Attempts to oxidize this substance have given only oily products.

When the acid melting at 179° was treated with methyl alcohol saturated with hydrogen chloride an oil and a very small quantity of a crystalline ester were formed. The acid undoubtedly loses carbon dioxide during esterification. Attempts to obtain this ester by oxidizing the ester of the acid melting at 185° were also unsuccessful. Under the conditions necessary for oxidation of the acid its ester is only partially oxidized, a considerable quantity being regained unchanged. The only products of oxidation are benzoic acid and an oil from which no pure substance has, as yet, been obtained.

There is, then, no proof of the structure of the acid melting at 179° and, therefore, from this work it is impossible to decide between formulas (1) and (2) advanced for the acid melting at 185° obtained by oxidation of the polymeric ethyl ester. An acid of either formula would be expected to give, on oxidation, the acid $C_{11}H_{10}O_5$.

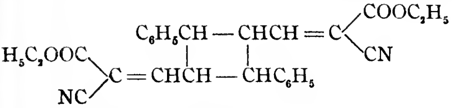
Reaction of Bromine on the Polymeric Ester Melting at 166°.—A chloroform solution of 5 grams of ester was cooled in a freezing mixture and 3.5 grams of bromine in the same solvent added slowly. The color of the bromine solution disappeared gradually. The solution remained at 0° for one week and the solvent was allowed to evaporate spontaneously. The residue, a heavy yellow oil, was stirred with a small quantity of methyl alcohol, cooled to 0°. Gradually a white, granular solid separated. This was filtered, washed with cold alcohol and recrystallized from hot methyl alcohol. It separates in shining white crystals, melting at 126°–127°. It is very readily soluble in acetone, chloroform and benzene; slightly soluble in cold alcohol and ether. The analyses show the substance to be a dibrom addition product:

0.1619 gram substance gave 0.3206 gram CO_2 and 0.0711 gram H_2O.

	Calculated for $C_{28}H_{26}O_4N_2Br_2$.	Found.
C	54.72	54.03
H	4.23	4.87

The alcohol washings from this product contained a small quantity of a volatile bromine compound which attacked the eyes. When poured into water the solution deposited a pasty mass containing bromine from which no pure compound could be obtained. The quantity of these secondary products was very small.

Isomerization of the Polymeric Ester (Melting at 166°) to Form Diethyl Diphenyltetramethylenebismethylenecyanacetate,



.—In one experiment for the preparation of the bromine compound just described, considerably less than the calculated quantity of bromine was used. The solution was treated exactly as before. A crystalline compound, which melted at 128°, separated from the methyl alcohol. This was found to contain no bromine and analyses showed it to be isomeric with the polymeric ester melting at 166°. The latter had, therefore, been transformed under the influence of bromine. The alcohol washings deposited a mixture of bromine compounds as before.

Diethyl diphenyltetramethylenebismethylenecyanacetate, melting at 128°, is readily soluble in benzene, chloroform, acetone and hot methyl and ethyl alcohols, slightly soluble in ether and ligroin. It may be purified by crystallization from alcohol, but better by solution in a small quantity of boiling benzene and addition of an equal volume of ligroin. From this it separates in small clumps of colorless compact crystals.

Analysis:

0.1509 gram substance gave 0.4101 gram CO_2 and 0.0800 gram H_2O.

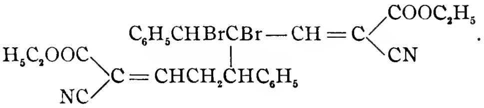
	Calculated for $C_{28}H_{26}O_4N_2$.	Found.
C	74.00	74.11
H	5.72	5.88

Molecular weight determined in boiling benzene (K = 26.1):

Grams solvent.	Gram substance.	Rise in boiling point.	Molecular weight.
33.08	0.1974	0°.035	446
	Calculated for $C_{28}H_{26}O_4N_2$,		454

The behavior of this compound is exactly like that of the polymeric methyl ester. It dissolves in concentrated sulphuric acid to a clear yellow solution from which water precipitates the colorless ester unchanged. On oxidation with potassium permanganate in acetone solution the products are α-truxillic, benzoic and oxalic acids. There can be, therefore, no doubt as to the structure of this compound.

The formation of this tetramethylene derivative from the high-melting polymeric ester by action of bromine makes most probable formula (I*a*) proposed for the latter compound, as was pointed out in the introduction, and, consequently, the formula (1) for the acid obtained by its oxidation. The dibrom addition product would have, accordingly, the structure



$$\begin{array}{l}\qquad\qquad\qquad \mathrm{C_6H_5CHBrCBr-CH=C{<}^{COOC_2H_5}_{CN}} \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \mathrm{{}^{H_5C_2OOC}_{NC}{>}C=CHCH_2CHC_6H_5} \end{array}.$$

It has not been possible to prepare again this tetramethylene derivative by this method. All attempts to duplicate the conditions of the reaction described have resulted in the formation of the bromine compound described above. The polymeric ester melting at 166° has been treated in chloroform and carbon tetrachloride solutions with bromine, iodine and hydrochloric acid in varying concentration, at 0°, at room temperature, in the dark and in the sunlight. In all cases the original ester or, with bromine, the dibrom addition product, have been the only substances isolated.

The compound has, however, been prepared by exposure to the light of the unstable ethyl α-cyancinnamylidenacetate.

Unstable Ethyl α-Cyancinnamylidenacetate.

Preparation.—The method used was that of Pfannl[1] for the mutual replacement of alkyl groups in esters of dibasic organic acids. This method was tried in order, if possible, to prepare from methyl cyancinnamylidenacetate an ethyl ester.

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[1] *Loc. cit.*

This might be expected to have the same configuration as the methyl ester, since the reaction takes place at room temperature, and, if so, would be isomeric with the ethyl ester already known if the assumption as to the difference in the reaction of these two compounds in the light is correct.

Five grams of the methyl ester were suspended in 500 cc. absolute ethyl alcohol and the calculated quantity of potassium (0.9 gram) in ethyl alcohol solution added slowly. The mixture was shaken for about an hour and a half until the methyl ester was all in solution. Dilute sulphuric acid was added in quantity sufficient to neutralize the solution and the solvent allowed to evaporate spontaneously. After one-half the alcohol had evaporated the residue was poured into water, the solid separating filtered, dried and dissolved in hot absolute alcohol. An ester separated in yellow needles which were washed with cold alcohol and again crystallized.

Properties.—The ester separates from concentrated solution in compact branching clumps somewhat different in appearance from the needles of the usual form. It is so much less soluble in alcohol than the latter that the two forms may be separated by fractional crystallization from alcohol.

On exposure to the light the ester decolorizes rapidly. The colorless product, washed with alcohol, crystallized from boiling alcohol in small compact crystals, melting at 128°. When melted with diethyl diphenyltetramethylenebismethylenecyanacetate, which had been prepared by isomerization of the polymeric ethyl ester melting at 166°, the two were found to be identical. This reaction proves that the ester obtained by the Pfannl reaction is not identical but isomeric with the ethyl α-cyancinnamylidenacetate previously known.

Each of the two ethyl esters melts at 113° and a mixture of the two at the same temperature, indicating that the new ester is unstable and changes over into the stable, usual form at or below its melting point. This was shown by dividing a portion of the new ester into two parts. One portion, (*A*), was exposed to the light. The other, (*B*), was melted, the product recrystallized from alcohol and then exposed. From (*A*) was obtained the polymer melting at 128°; from (*B*) that melting at 166°. The new ester is, therefore, the unstable form.

To distinguish between these isomeric esters, the best method is to expose small quantities of each to the light and compare the products formed. This can be done with extremely small amounts, as the polymers may be distinguished from each other in minute quantities by the reaction with concentrated sulphuric acid. The low-melting compound dissolves slowly in the acid. The solution is a clear yellow. The high-melting compound dissolves instantly to form a brilliant crimson solution.

The quantity of unstable ester obtained in this reaction was small. It is hoped that it may be possible to perfect the method so that larger yields of the substance may be obtained and studied further. It is possible that this method may be found to be of value for the preparation of other esters which are unstable, and, therefore, not obtained under the usual conditions of ester formation.

CHEMICAL LABORATORY,
BARNARD COLLEGE,
Feb., 1911.

[Contributions from the Sheffield Laboratory of Yale University.]

CXCI.—ALKYLATION OF AROMATIC AMINO ACIDS: 3-AMINO-2,4-DIMETHYLBENZOIC ACID.

BY HENRY L. WHEELER AND CHARLES HOFFMAN.

[FIFTH PAPER.]

Our previous papers on the alkylation of aromatic amino acids have been published in THIS JOURNAL.[1]

In regard to the methylaminobenzoic acids, we found that 2-amino-3-methylbenzoic acid (I), which is represented in Beilstein's *Handbuch*[2] as "4-Aminotoluylsäure" (2-amino-5-methylbenzoic acid), was readily alkylated when warmed with four molecular proportions of potassium hydroxide and five of alkyl halide in alcoholic solution.

The products with ethyl iodide were *N*-monoethylamino

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[1] **42**, 455 (1909); **43**, 398 (1910); **44**, 113, 441 (1910).

[2] III, **2**, 1337.

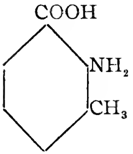
acid (15 parts), *N*-diethylamino acid (1 part) and a small amount of *O*-ester (2 parts). The alkylation therefore, in this case, took place for the greater part on the nitrogen.[1] The structure of this amino acid appears to have now been definitely settled as 2-amino-3-methylbenzoic acid ("2-Amino-*m*-toluylsäure") by Findeklee[2] and Müller.[3]

We may add, in confirmation of this, that the acid on distilling with calcium oxide gives *o*-toluidine. If the acid were 2-amino-5-methylbenzoic acid, as previously represented, it would yield *p*-toluidine by this treatment.

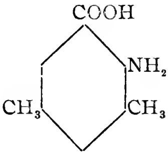
2-Amino-3,5-dimethylbenzoic acid (II) has an analogous structure to that of the above acid, inasmuch as the amino group is situated between the $—CH_3$ and —COOH groups, and on alkylation it behaves in a similar manner.[4]

With ethyl iodide and alkali the products were *N*-diethylamino acid (30 parts), *N*-monoethylamino acid (10 parts), a small amount of ester (1 part), and unaltered acid (5 parts).

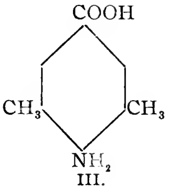
4-Amino-3,5-dimethylbenzoic acid (III) reacted, under the same conditions, in an entirely different and abnormal manner on alkylation. In this case only the ethyl ester (42 per cent.) and unaltered acid was obtained.[5]



I.



II.



III.

With these results it was of interest to examine the behavior of the isomeric 3-amino-2,4-dimethylbenzoic acid (VIII), which, like the preceding acid (III), has the amino radical surrounded by methyl groups. This has now been done and

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[1] This Journal, **44**, 123 (1910).

[2] Ber. d. chem. Ges., **38**, 3553 (1905).

[3] *Ibid.*, **42**, 430 (1909).

[4] This Journal, **44**, 121 (1910).

[5] *Ibid.*, **44**, 120 (1910).

we find that 3-amino-2,4-dimethylbenzoic acid reacts with both methyl and ethyl iodides like 4-amino-3,5-dimethylbenzoic acid, since it alkylates with difficulty and esters are the chief products. For example, with ethyl iodide we obtained the *O*-ester (4.5 parts), unaltered acid (5.5 parts), and a little of the *N*-monoethyl acid (1 part).

These results afford further evidence that methyl groups adjacent to an amino group interfere with the normal alkylation of this radical in amino acids, while the curious fact remains that a methyl group and a carboxyl in these positions permit the alkylation to take place normally with the formation of *N*-alkyl derivatives as the main products. The introduction of negative groups causes the *O*-esters to again predominate; 5-iod-2-amino-3-methylbenzoic acid[1] gives mainly the *O*-ester, the ratio of ester to *N*-alkyl acid being 15 : 4, while 2,4,6-tribrom-3-aminobenzoic acid yields exclusively the *O*-ester.

3-Amino-2,4-dimethylbenzoic acid is new. It was prepared as follows: 2,4-Dimethylbenzoic acid (IV) was nitrated and the resulting 3,5-dinitro-2,4-dimethylbenzoic acid (V) was reduced by means of ammoniom sulphide. This reagent reduced only the nitro group in the 5-position, giving 3-nitro-5-amino-2,4-dimethylbenzoic acid (VI). When this acid was diazotized and treated with alcohol the amino group was removed and 3-nitro-2,4-dimethylbenzoic acid (VII) was obtained. Then, on reducing with ferrous sulphate and ammonia, 3-amino-2,4-dimethylbenzoic acid (VIII) was formed. The yields were practically quantitative in each step except the preparation of 3-nitro-2,4-dimethylbenzoic acid, in which case the amount of material obtained was 70 per cent. of the calculated. The preparation of 3-nitro- and 3-aminoxylic acid by this method is therefore a simple matter.

Claus[2] believed that he had obtained 3-nitro-2,4-dimethylbenzoic acid by oxidizing 3-nitro-2,4-dimethylphenylmethyl ketone, a by-product difficult to purify which was formed

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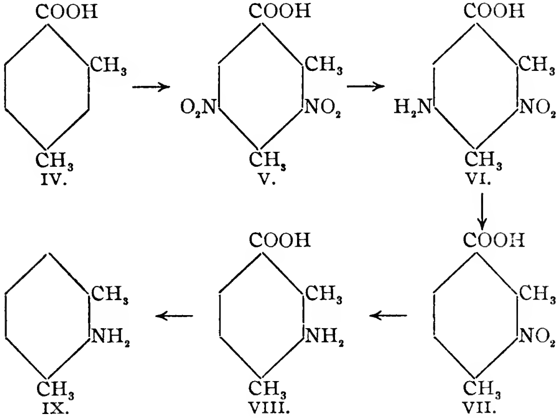
[1] This Journal, **44,** 116 (1910). Previously represented as 3-iod-2-amino-5-methylbenzoic acid.

[2] J. prakt. Chem., [2] **41,** 500 (1890).

in small amount in the nitration of 2,4-dimethylphenylmethyl ketone. The melting point he assigns to 3-nitroxylic acid (135°) is 44° lower than that of our acid.

The structure of our nitro and amino acids (VII and VIII) was shown on distilling the amino acid with calcium oxide, whereupon *vic.-m*-xylidine or 2-amino-1,3-xylene (IX) was obtained. This oil was identified by means of its acetyl derivative. The synthesis may be represented as follows:



Since the above reactions are smooth throughout, they might be employed for the preparation of *vic.-m*-xylidine free from isomers. This base is now usually obtained by separating it, in a number of ways, from the commercial mixture of xylidines in which it occurs in small amount (about 2.7 per cent.[1]).

EXPERIMENTAL PART.

3,5-Dinitro-2,4-dimethylbenzoic Acid.—This acid has been prepared by Frey and Horowitz,[2] who nitrated 2,4-dimethylbenzoic acid, using 10 parts of nitric acid (specific gravity

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[1] Hodgkinson and Limpach: J. Chem. Soc., **77**, 67.

[2] J. prakt. Chem., [2] **43**, 120 (1891).

1.4) and 30 parts of concentrated sulphuric acid. They do not give the yield.

We found that the following procedure gave a yield of 95 per cent. of the calculated. 2,4-Dimethylbenzoic acid was prepared according to the method of Bouveault.[1] Seventy grams of xylene gave 60 grams of pure acid.

Thirty cc. of concentrated nitric acid (specific gravity 1.4) were mixed with 45 cc. of concentrated sulphuric acid and 15 grams of *m*-xylic acid were slowly added to this mixture at the temperature of the room. When all the acid was added a violent reaction took place, after which the mixture was heated for 3 hours on the steam bath. The crystalline product that separated, on pouring into water, was washed and dried; it weighed 23 grams and melted at 195°.

3-Nitro-5-amino-2,4-dimethylbenzoic Acid.—This new acid was prepared as follows: Twenty grams of the above dinitro acid were added to a mixture of 150 cc. of concentrated ammonium hydroxide and 100 cc. of alcohol. The mixture was saturated with hydrogen sulphide at ordinary temperature and then warmed on the water bath under a return condenser for a half hour. It was then cooled, saturated again with hydrogen sulphide and reheated an hour longer on the steam bath. The alcohol and excess of ammonia were evaporated and the filtered solution was precipitated with dilute hydrochloric acid, avoiding an excess since the amino acid is soluble in hydrochloric acid. It is not precipitated by acetic acid. The yield of crude product, which melted with decomposition at 240°, was 16.5 grams, or 95 per cent. of the calculated. It crystallized from alcohol in beautiful, straw-colored prisms which are difficultly soluble in water. Three crystallizations gave a product melting to a dark oil at 251°.

	Calculated for $C_9H_{10}O_4N_2$.	Found.
N	13.33	13.26

The *hydrochloride*, $C_9H_{10}O_4N_2.HCl$, was obtained on crystallizing the acid from dilute hydrochloric acid. It formed

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[1] Bull. soc. chim., [3] **17**, 363.

clusters of large, spikelike prisms which melted at 250°, with effervescence.

	Calculated for $C_9H_{11}O_4N_2Cl$.	Found.
N	11.36	10.97

The *acetyl derivative* was formed by treating the amino acid with acetyl chloride. It is moderately soluble in water, readily in hot alcohol, and it crystallizes in colorless needles which melt to a dark oil at 247°. When mixed with unaltered acid the melting point was lowered to 200°.

	Calculated for $C_{11}H_{12}O_5N_2$.	Found.
N	11.11	11.00

3-Nitro-2,4-dimethylbenzoic Acid.—Fifteen grams of 3-nitro-5-amino-2,4-dimethylbenzoic acid were dissolved at 0° in 24 cc. of concentrated sulphuric acid, by grinding in a mortar, and fourteen grams of dry sodium nitrite were added. The thick, pasty mass which formed was poured upon crushed ice; this gave a yellow diazo solution. It was filtered into 200 cc. of boiling alcohol and the heating was continued until the dark red color which formed at first had practically disappeared. When the solution was poured upon crushed ice, 9 grams of crude acid, or 70 per cent. of the calculated, separated. This acid is difficultly soluble in hot water, readily in alcohol and only moderately soluble in benzene. It crystallizes from the latter solvent in pointed prisms having a light brown color and melting at 179°. Claus[1] describes this compound as melting at 135°.

	Calculated for $C_9H_9O_4N$.	Found.
N	7.18	7.17

The *amide*, $C_8H_8NO_2.CONH_2$, obtained by treating the acid with phosphorus pentachloride and then pouring the product upon solid ammonium carbonate, crystallized from water in plates and melted at 138°.

	Calculated for $C_9H_{10}O_3N_2$.	Found.
N	14.43	14.10

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[1] *Loc. cit.*

3-Amino-2,4-dimethylbenzoic Acid.—Ten grams of 3-nitro-2,4-dimethylbenzoic acid were dissolved in 125 cc. of concentrated ammonium hydroxide and 125 grams of ferrous sulphate (calculated for 8 moles), dissolved in 200 cc. of water, were added. This mixture was then heated on the steam bath for one hour, after which it was filtered and the filtrate concentrated to a small volume. It was then acidified with dilute acetic acid and, on standing for some time, the separation of amino acid was complete. The yield of crude product was 7.5 grams or 93 per cent. of the calculated. When crystallized twice from water it formed needles or prisms, the crystalline form depending on the concentration, and it melted to a brown oil at 146°. Its solution in water or dilute alcohol shows a green fluorescence. It is readily soluble in ethyl acetate, alcohol and benzene.

	Calculated for $C_9H_{11}O_2N$.	Found. I.	II.
N	8.48	8.46	8.79

The *acetyl derivative*, $C_9H_9O_2NHCOCH_3$, was formed by treating the acid with acetic anhydride. It crystallized from alcohol in needles which melted with decomposition at 243°. It is moderately soluble in warm water and readily soluble in dilute alcohol.

	Calculated for $C_{11}H_{13}O_3N$.	Found.
N	6.76	6.93

vic.-m-*Xylidine* was obtained from 2,4-dimethyl-3-aminobenzoic acid when the acid was mixed with an equal weight of calcium oxide and the mixture distilled on the sand bath. The oil obtained was treated with an excess of acetic anhydride. Upon cooling, the crystalline substance that separated was crystallized twice from water. It melted at 175°. The melting point of 1,3-dimethyl-2-acetanilide (*vic.-m*-acetxylidide) is variously given from 174°–176°; that of 2,4-dimethylacetanilide at 129°; while the other theoretically possible dimethylacetanilide, namely 3,5-dimethylacetanilide, has been found, by different observers, to melt at 138°, 140°.5 and 144°.5.

	Calculated for $C_{10}H_{13}ON$.	Found.
N	8.59	8.45

3-Iod-2,4-dimethylbenzoic Acid.—Four and eight-tenths grams of the above amino acid, 25 cc. of sulphuric acid, and 4.3 grams of dry sodium nitrite (calculated for 2 moles) were mixed in the cold and poured upon crushed ice. The diazo solution was filtered into an excess of potassium iodide (30 grams) dissolved in water; on warming, and then treating the product with acid sodium sulphite, 6 grams, or 75 per cent. of the calculated, of crude iod acid was obtained. It crystallized from dilute alcohol in needlelike prisms which, after three crystallizations, melted at 167°. It is readily soluble in alcohol and benzene.

	Calculated for $C_9H_9O_2I$.	Found.
I	46.01	45.88

Ethylation of 3-Amino-2,4-dimethylbenzoic Acid.—Five grams of the acid, 7 grams of potassium hydroxide (4 moles) in alcoholic solution and 22 grams of ethyl iodide (5 moles) were mixed and the whole heated under a return condenser for 2 hours. The alcohol was then evaporated and the residue taken up in water. An oil remained which did not solidify on cooling in a freezing mixture. It was extracted with ether and the ether solution was shaken with dilute ammonium hydroxide. Upon evaporating the ether 1.8 grams of oil were obtained which did not crystallize. This proved to be the primary amino ester, since on boiling with alcoholic potassium hydroxide 3-amino-2,4-dimethylbenzoic acid was obtained. On evaporating the alcoholic solution, taking the residue up in water and precipitating with acetic acid, the precipitated acid melted at 146° and, when mixed with unaltered acid, the melting point was not changed.

The ammonia solution was evaporated to dryness and the residue extracted with ethyl acetate, which, upon evaporation, gave 0.4 gram of oil. This oil dissolved in dilute hydrochloric acid, and gave a precipitate when cooled to 0° and a few drops of dilute sodium nitrite were added.

The water solution from the first extraction was acidified with acetic acid, evaporated to dryness, and the residue was extracted with ethyl acetate, whereupon 2.2 grams of unaltered acid melting at 146° were obtained. When mixed with unaltered acid the melting point remained the same.

Methylation of 3-Amino-2,4-dimethylbenzoic Acid.—The proportions of acid, alkali and alkyl halide were the same as in the previous experiment. Methyl alcohol was used in place of ethyl alcohol, the other conditions being the same. On evaporating the alcohol an oil was again obtained in this case. This partially solidified on cooling. The residue was extracted with water and from this solution 3.2 grams of unaltered acid were recovered on acidifying with acetic acid.

The residue insoluble in water was extracted with dilute ammonia and ether. On evaporating the ether 0.7 gram of oil was obtained, which, on saponification, gave unaltered acid melting at 146°.

The ammonia solution was acidified with acetic acid, after evaporation, and one gram of substance was obtained which, on crystallizing from water, melted at 146°.

The mother liquor from this crystallization, on acidifying with hydrochloric acid, cooling to 0° and adding dilute sodium nitrite, gave a crystalline precipitate. This was filtered and washed with water to remove all the sodium nitrite. A small portion was added to a solution of diphenylamine in concentrated sulphuric acid. An intense blue color was immediately formed, showing the presence of a nitroso compound and therefore the formation of 3-methylamino-2,4-dimethylbenzoic acid in this alkylation.

Methylation of 2,4,6-Tribrom-3-aminobenzoic Acid.

Methyl 2,4,6-Tribrom-3-aminobenzoate.—Eight grams of the acid, 1.74 grams of potassium hydroxide (calculated for 1.5 moles) in 50 cc. of methyl alcohol and 12.1 grams of methyl iodide (2 moles) were mixed and warmed for 15 hours. On evaporating the alcohol and treating the residue with 100 cc. of water a gummy residue remained, which, on drying, weighed 3.2 grams. This was insoluble in alkali and on crystallizing from alcohol, in which it is readily soluble, colorless needles melting at 93°–94° were obtained. A nitrogen determination agreed with the calculated for a methyl ester, and on saponifying with alcoholic potassium hydroxide the unaltered acid was obtained.

	Calculated for $C_8H_6O_2NBr_3$.	Found.
N	3.66	3.57

The aqueous solution or extract mentioned above, on acidifying with hydrochloric acid, gave 4.1 grams of unaltered acid melting at 168°–169°. In this experiment 38 per cent. of the acid was converted into ester.

In another experiment the same proportions were used, only the time of heating was shortened to 3 or 4 hours. This gave 17 per cent. of ester and 80 per cent. of unaltered acid was recovered.

o-*Toluidine from 2-Amino-3-methylbenzoic Acid.*—The base was obtained by distilling the acid with an equal weight of calcium oxide. The acid was obtained as follows: *m*-Toluic acid was nitrated and the chief product, melting at 219°–220°, was reduced with ferrous sulphate and ammonia. This gave the amino acid melting at 172°.

Since we also obtained the nitro acid melting at 211° in the nitration of *m*-toluic acid, and this material was shown to be the 4-nitro-3-methylbenzoic acid by converting it into the amide melting at 151°,[1] and since there are only two mononitro-*m*-toluic acids with the nitro group ortho to methyl, it follows that the amino acid used by us, and melting at 172°, was 2-amino-3-methylbenzoic acid.[2]

The *o*-toluidine obtained was converted into the acetyl derivative. It melted at 110° and a nitrogen determination gave 9.20 per cent. nitrogen while the calculated is 9.39 per cent.

New Haven, Conn.,
January, 1911.

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[1] Beilstein and Kreusler: Ann. Chem. (Liebig), **144**, 168.

[2] Wheeler and Hofman: This Journal, **44**, 113 (1910).

[Contributions from the Sheffield Laboratory of Yale University.]

CXCII.—ON HYDANTOINS:

ALDEHYDE CONDENSATION PRODUCTS OF PHENYLTHIOHYDANTOINS.

By Henry L. Wheeler and Charles A. Brautlecht.

[SECOND PAPER.]

We have shown in our first paper[1] that hydantoin condenses with aldehydes on warming with anhydrous sodium acetate in glacial acetic acid.

We found also that 1-phenylhydantoin reacts in the same manner, but we observed no condensation when 3-phenyl- or 1,3-diphenylhydantoin was employed.

Erlenmeyer had previously stated that phenylhydantoin does not condense with benzaldehyde when warmed with acetic anhydride and fused sodium acetate.[2]

The failure of two of these types of hydantoins to condense with aldehydes might seem to be due to the presence of a phenyl group in the 3-position, or in other words, to the absence of the grouping $C=N—CH_2—C=O$, and, if this were true, then it would be expected from analogy that the corresponding normal thiohydantoins would behave in a similar manner.

We have now investigated the tendency of 1-phenyl-2-thiohydantoin (I), 2-thio-3-phenylhydantoin (II) and 2-thio-1,3-diphenylhydantoin (III) to react with aldehydes and have made the curious observation that not only does 2-thio-1-phenylhydantoin condense apparently more readily than hydantoin or the corresponding *O*-derivative, but also that both of the other types of thiohydantoins, having phenyl groups in the 3-position, readily give condensation products.

These results afford further evidence that the grouping $C=N—CH_2—C=O$ is not necessary to render the methylene hydrogen in hydantoins reactive towards aldehydes. This

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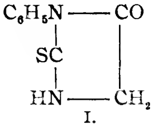
[1] Wheeler and Hoffman: This Journal, **45**, 368.

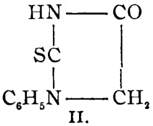
[2] Ann. Chem. (Liebig), **307**, 73 (1899).

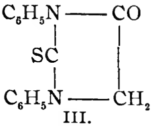
grouping has been discussed in this connection by Erlenmeyer, Junior,[1] although he found that creatine,

$$H_2N—C(:NH)—N(CH_3)CH_2COOH,$$

readily undergoes condensation with benzaldehyde.[2]

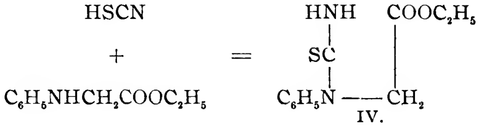

I.


II.

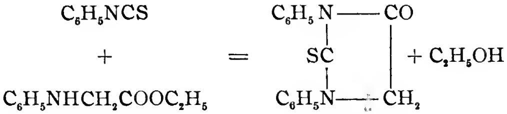

III.

2-Thio-1-phenylhydantoin (I) was prepared by combining glycine or its ethyl ester in alkaline solution with phenyl mustard oil.[3]

2-Thio-3-phenylhydantoin (II), which represents a new type of thiohydantoins, was prepared by warming the hydrochloric acid salt of phenylglycine ester with potassium thiocyanate; the resulting product, the thiohydantoic ester (IV), on warming with hydrochloric acid, gave the hydantoin.


IV.

2-Thio-1,3-diphenylhydantoin (III), another new type, was prepared by heating phenylglycine ethyl ester (or phenylglycine) with phenyl mustard oil.



The condensation of hydantoins with aldehydes takes place with the separation of one molecular proportion of water, and since it makes no difference, in the case of thiohydantoins,.

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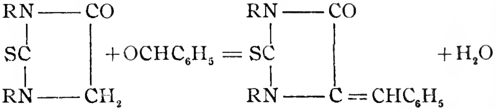
[1] Ann. Chem. (Liebig), **337,** 205 (1904).

[2] *Ibid.*, **284,** 49 (1895).

[3] Aschan: Ber. d. chem. Ges., **17,** 420 (1884). Marckwald, Neumark and Stelzner: *Ibid.*, **24,** 3278 (1891).

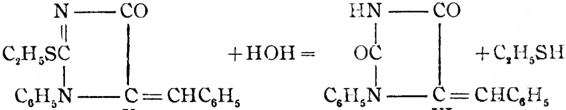
whether or not the hydrogen atoms attached to nitrogen are replaced by the phenyl group, it is evident that these hydrogen atoms take no part in the condensation. For example, the general reaction with benzaldehyde, in which R is either H or C_6H_5, is represented as follows:



$$\begin{matrix}\mathrm{RN}&—&\mathrm{CO}\\ |&&|\\ \mathrm{SC}&&|\\ |&&|\\ \mathrm{RN}&—&\mathrm{CH_2}\end{matrix} + \mathrm{OCHC_6H_5} = \begin{matrix}\mathrm{RN}&—&\mathrm{CO}\\ |&&|\\ \mathrm{SC}&&|\\ |&&|\\ \mathrm{RN}&—&\mathrm{C{=}CHC_6H_5}\end{matrix} + \mathrm{H_2O}$$

We intend to give a description of the chemical behavior of the aldehyde condensation products of thiohydantoins in later papers. It may be stated here, however, that both 2-thio-1-phenyl- and 2-thio-3-phenylhydantoins give 2-mercapto derivatives when warmed with alkali and alkyl halide. 2-Ethylmercapto-1-phenylanisalhydantoin, on boiling with hydrochloric acid, gives off mercaptan and yields 1-phenylanisalhydantoin. The product is identical with that resulting from the condensation of anisaldehyde with 1-phenylhydantoin.

When 2-ethylmercapto-3-phenylbenzalhydantoin (V) was boiled with hydrochloric acid it was likewise desulphurized and 3-phenylbenzalhydantoin (VI), which was not obtained by direct condensation, was formed:

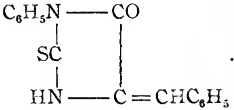


$$\begin{matrix}&\mathrm{N}&—&\mathrm{CO}\\ &\|&&|\\ \mathrm{C_2H_5}&\mathrm{SC}&&|\\ &|&&|\\ \mathrm{C_6H_5}&\mathrm{N}&—&\mathrm{C{=}CHC_6H_5}\end{matrix} + \mathrm{HOH} = \begin{matrix}&\mathrm{HN}&—&\mathrm{CO}\\ &|&&|\\ &\mathrm{OC}&&|\\ &|&&|\\ \mathrm{C_6H_5}&\mathrm{N}&—&\mathrm{C{=}CHC_6H_5}\end{matrix} + \mathrm{C_2H_5SH}$$

V. VI.

EXPERIMENTAL PART.

2-Thio-1-phenylbenzalhydantoin,



$$\begin{matrix}\mathrm{C_6H_5N}&—&\mathrm{CO}\\ |&&|\\ \mathrm{SC}&&|\\ |&&|\\ \mathrm{HN}&—&\mathrm{C{=}CHC_6H_5}\end{matrix}$$

.—In these condensations we have taken 1 part of phenylthiohydantion, 2 parts of fused sodium acetate and a little over the calculated amount for 1 molecular proportion of aldehyde, the excess being from one-seventh to one-tenth of the calculated. The mixture was dissolved in 14 parts of glacial acetic acid and boiled from 1–2 hours. The addition of acetic anhydride was neither necessary nor advisable. In this case, from 10 grams of thio-1-phenyhydantoin with benzaldehyde, after heating for a short time, some of the condensation product separated from the hot solution. On cooling, water was added and the precipitated crude material was washed with water. When dry it weighed 14.6 grams, or the theoretical amount.

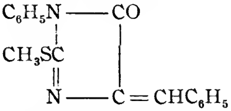
2-Thio-1-phenylbenzalhydantoin crystallized from alcohol in the form of yellow prisms, which melted to a clear oil at 204°. It was soluble in about 60 parts of boiling alcohol, practically insoluble in cold water but readily soluble in alkali with orange-yellow color. If dissolved in alkali without warming, and acetic acid or hydrochloric acid precipitated the unaltered hydantoin melting at 204°. When it was boiled for a few minutes in normal potassium hydroxide and then precipitated with hydrochloric acid at 0°, some hydrogen sulphide was noticed and a salmon-colored precipitate resulted. This melted with effervescence at 186°–188°. When this material was recrystallized from alcohol the hydantoin melting at 204° was obtained. The precipitate was therefore in all probability thiophenylbenzalhydantoic acid,

$$C_6H_5NHCSNHC(:CHC_6H_5)COOH.$$

The thiophenylbenzalhydantoin was crystallized twice from alcohol and dried at 110° for analysis:

	Calculated for $C_{16}H_{12}ON_2S$.	Found.
N	10.00	10.07

2-Methylmercapto-1-phenylbenzalhydantoin,

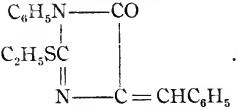


$$\begin{array}{l} C_6H_5N \text{---} CO \\ CH_3SC \qquad \vert \\ N \text{---} C = CHC_6H_5 \end{array}$$

.—2-Thio-1-phenylbenzalhydantoin was dissolved in methyl alcohol containing one molecular proportion of sodium methylate and 1.5 times the calculated amount of methyl iodide was added. The reaction took place at ordinary temperature, the solution became deep ruby-red, and in a few minutes cream-colored, needlelike prisms separated, which on standing in the mother liquor for a few hours changed into compact octahedral blocks or pyramids. Both forms melted to a clear oil at 150° and when mixed the melting point was not altered. The change in form was only observed in the reaction mixture and not on crystallizing from ethyl or methyl alcohol. The yield of crude material, after evaporating the alcohol and washing with water, was quantitative.

	Calculated for $C_{17}H_{14}ON_2S$.	Found.
N	9.52	9.49

2-Ethylmercapto-1-phenylbenzalhydantoin,



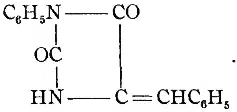
.—The solution of 2-thio-1-phenylbenzalhydantoin in alcohol containing one molecular proportion of sodium ethylate and two of ethyl bromide was warmed for a short time, or until it became neutral. On cooling, the material that separated was washed with water and recrystallized from alcohol. It formed straw-yellow needles, which melted to a clear oil at 123°.

	Calculated for $C_{18}H_{16}ON_2S$.	Found.
N	9.09	9.01

2-Benzylmercapto-1-phenylbenzalhydantoin was obtained by shaking the thiohydantoin in 20 per cent. potassium hydroxide solution with benzyl chloride. After washing with water and crystallizing from alcohol it gave almost colorless needles, melting to a clear oil at 178°–179°. Like the above methyl and ethylmercapto derivatives this substance was practically insoluble in water and cold dilute sodium hydroxide. It dissolved in about 890 parts alcohol at 22° and in about 137 parts of boiling alcohol.

	Calculated for $C_{23}H_{18}ON_2S$.	Found.
N	7.57	7.53

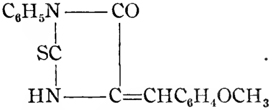
1-Phenylbenzalhydantoin,



.—When the above mercapto derivatives are boiled with concentrated hydrochloric acid diluted with alcohol, mercaptan is evolved practically quantitatively. The phenylbenzalhydantoin crystallizes from alcohol in pale, cream-colored, twinned prisms or diamond-shaped blocks which melt to a clear oil at 243°.

	Calculated for $C_{16}H_{12}O_2N_2$.	Found.
N	10.61	10.57

2-Thio-1-phenylanisalhydantoin,



.—This was prepared from anisaldehyde and thio-1-phenylhydantoin; the yield was almost quantitative. It is practically insoluble in cold water and difficultly soluble in benzene. It is readily soluble in hot glacial acetic acid. It dissolves in about 124 parts of boiling alcohol and on cooling crystallizes in long, lemon-yellow needles melting at 214°.

	Calculated for $C_{17}H_{14}O_2N_2S$.	Found.
N	9.03	8.97

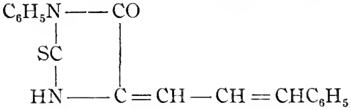
This hydantoin dissolves in dilute sodium hydroxide and gives a yellow, difficultly soluble sodium salt which crystallizes in plates and melts with decomposition at about 280°.

2-Ethylmercapto-1-phenylanisalhydantoin, from the above, sodium ethylate and an excess of ethyl bromide, formed canary-yellow needles melting at 138°–139°, when crystallized from about 25 parts of alcohol.

	Calculated for $C_{19}H_{18}O_2N_2S$.	Found.
N	8.28	8.16

When this mercapto derivative was desulphurized by boiling with concentrated hydrochloric acid and alcohol, ethyl mercaptan was evolved and a quantitative yield of 1-phenylanisalhydantoin was obtained. This melted at 151°–152°[1] and proved to be identical with the product obtained by condensing hydantoin and anisaldehyde.

2-Thio-1-phenylcinnamylhydantoin,

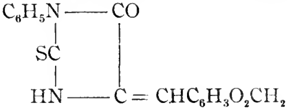


$$\begin{array}{lll} C_6H_5N & \text{---} & CO \\ \quad | & & | \\ \quad SC & & | \\ \quad | & & | \\ HN & \text{---} & C=CH-CH=CHC_6H_5 \end{array}$$

, was obtained from thio-1-phenylhydantoin and cinnamaldehyde. The yield of crude product was 93.6 per cent. of the calculated. When crystallized from alcohol or glacial acetic acid it formed long, orange-colored, flat prisms melting to a dark brown oil at 272°–273°. It is practically insoluble in water and one part dissolves in about 305 parts of boiling alcohol. It is insoluble in ether and difficultly soluble in benzene. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid, giving an intense red color, and is precipitated unaltered from this solution on adding water.

	Calculated for $C_{18}H_{14}ON_2S$.	Found.
N	9.15	9.09

2-Thio-1-phenylpiperonalhydantoin,



$$\begin{array}{lll} C_6H_5N & \text{---} & CO \\ \quad | & & | \\ \quad SC & & | \\ \quad | & & | \\ HN & \text{---} & C=CHC_6H_3O_2CH_2 \end{array}$$

, from thio-1-phenylhydantoin and piperonaldehyde, formed yellow plates melting at 222°–

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[1] Wheeler and Hoffman: THIS JOURNAL, **45**, 368.

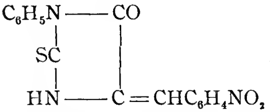
223°. It was crystallized from 28 parts of glacial acetic acid and then from hot alcohol in which it is more difficultly soluble. The yield of crude product that separated directly on adding water after condensation was 84 per cent. of the calculated, while more was obtained from the acetic acid filtrate on evaporating and treating the residue with water.

	Calculated for $C_{17}H_{12}O_3N_2S$.	Found.
N	8.64	8.64

When this hydantoin was dissolved in 20 parts of warm normal potassium hydroxide and the solution cooled, beautiful long yellow needles separated which gave results on analysis agreeing with those calculated for a potassium salt of the hydantoin and not for the hydantoic acid.

	Calculated for $C_{17}H_{11}O_3N_2SK$.	Found.
K	10.77	10.59

*2-Thio-1-phenyl-*p*-nitrobenzalhydantoin,*

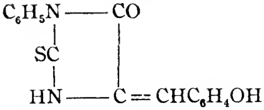


.—The condensation of *p*-nitrobenzaldehyde with thio-1-phenylhydantoin gave a very difficultly soluble product. For analysis it was crystallized from glacial acetic acid, then washed with alcohol and dried at 100°. It formed lemon-yellow, flat, pointed prisms which melted at about 278°–279°.

	Calculated for $C_{16}H_{11}O_3N_3S$.	Found.
N	12.92	12.90

This hydantoin is difficultly soluble in an excess of sodium hydroxide, owing to the formation of a rather insoluble sodium salt. It may be precipitated unaltered from its solution by hydrochloric acid.

2-Thio-1-phenylsalicylhydantoin,

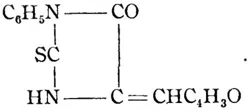


, formed straw-yellow prisms melting at 224°–225°, when crystallized from glacial acetic acid and alcohol.

	Calculated for $C_{16}H_{12}O_2N_2S$.	Found.
N	9.45	9.51

Thio-1-phenylsalicylhydantoin dissolved in sodium hydroxide, forming an intense orange-red solution, and hydrochloric acid reprecipitated the unaltered hydantoin. It is practically insoluble in ether and water and difficultly soluble in alcohol.

2-Thio-1-phenylfurfuralhydantoin,



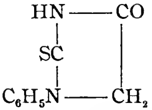
.—The condensation product of furfuraldehyde with thio-1-phenylhydantoin formed yellow prismatic blocks, melting at 233°–234°, when crystallized from glacial acetic acid. It is difficultly soluble in alcohol and it dissolves in concentrated sulphuric acid, forming a yellow solution which changes to a dark green.

	Calculated for $C_{14}H_{10}O_2N_2S$.	Found.
N	10.37	10.40

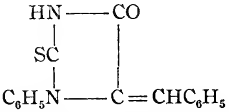
Ethyl Phenylaminoacetate Hydrochloride, $HCl.C_6H_5NHCH_2COOC_2H_5$.—This salt, which appears to be new, was prepared by dissolving phenylglycine ester in dry ether and then saturating the solution with dry hydrogen chloride. The solution became warm and an oily precipitate first separated which soon changed to a white crystalline mass. This was washed with ether and dried over potassium hydroxide in a vacuum desiccator. It could be crystallized by dissolving in absolute alcohol and precipitating with ether. It then formed colorless plates which melted at about 119°.

	Calculated for $C_{10}H_{14}O_2NCl$.	Found.
Cl	16.47	16.32

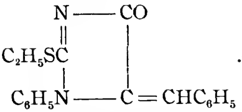
On standing or on warming the salt turns green and decomposes.

2-Thio-3-phenylhydantoin,  .—The above salt was dissolved in absolute alcohol containing a slight excess over the calculated of potassium thiocyanate and the solution boiled for about 4 hours. On evaporating the solution an oil was obtained in addition to potassium chloride and the excess of potassium thiocyanate. This residue was heated for two hours longer on the steam bath, then dissolved in alcohol and warmed with a little dilute hydrochloric acid. On evaporating the alcohol, crystalline material was obtained. This crystallized from 12 parts of boiling alcohol in beautiful, practically colorless, transparent prisms melting at 179°–180°.

	Calculated for $C_9H_8ON_2S$.	Found.
N	14.58	14.47

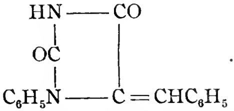
2-Thio-3-phenylbenzalhydantoin,  .—The condensation of 2-thio-3-phenylhydantoin with benzaldehyde was carried out as follows: The hydantoin was dissolved in 6 parts of boiling glacial acetic acid containing 2 parts of fused sodium acetate, a slight excess of benzaldehyde was added and the mixture boiled for one and a half hours. On adding water and crystallizing the precipitated material from alcohol, yellow plates were obtained melting to a brownish yellow oil at 207°–208°.

	Calculated for $C_{16}H_{12}ON_2S$.	Found.
N	10.00	10.01



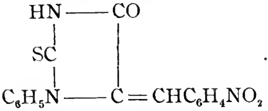
2-Ethylmercapto-3-phenylbenzalhydantoin, .—Five grams of the above condensation product were converted into the ethylmercapto derivative in the same manner as in the case of the isomeric 1-phenyl compound. The product was practically insoluble in water and somewhat difficultly soluble in alcohol, from which solvent it formed yellow prisms melting to a clear oil at 165°–166°.

	Calculated for $C_{18}H_{16}ON_2S$.	Found. I.	II.
N	9.09	9.01	9.15



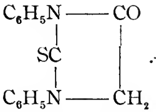
3-Phenylbenzalhydantoin, .—When the above mercapto derivative was boiled with a mixture of alcohol and concentrated hydrochloric acid, mercaptan was evolved. After digesting on the steam bath for a number of hours, then evaporating to dryness, washing the residue with ether and crystallizing from alcohol, pale yellow plates were obtained which melted to a clear oil at 223°–224°.

	Calculated for $C_{16}H_{12}O_2N_2$.	Found. I.	II.
N	10.61	10.55	10.48



*2-Thio-3-phenyl-*p*-nitrobenzalhydantoin*, .—The condensation of 2-thio-3 phenylhydantoin with *p*-nitrobenzaldehyde was carried out in the same manner as with benzaldehyde. The yield of crude product was 92 per cent. of the calculated. It crystallized from 21 parts of hot glacial acetic acid and 35 parts of hot alcohol in orange-red prisms, which melted to a clear oil at 236°–237°.

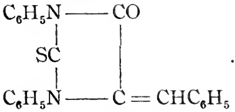
	Calculated for $C_{16}H_{11}O_3N_3S$.	Found. I.	Found. II.
N	12.92	12.89	12.81

2-Thio-1,3-diphenylhydantoin,  .—This was prepared by heating phenylglycine or its ethyl ester with phenyl mustard oil in an oil bath at 150° until water or alcohol ceased being evolved. The yields were nearly quantitative. The diphenylthiohydantoin was crystallized from 50 parts of boiling alcohol, whereupon flat yellow prisms melting to a clear oil at 212° were obtained.

	Calculated for $C_{15}H_{12}ON_2S$.	Found.
N	10.45	10.46

This hydantoin was found to be soluble in warm dilute sodium hydroxide, yielding an orange-yellow solution, from which it separated unaltered on adding an excess of hydrochloric acid.

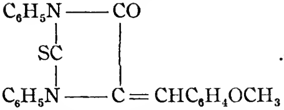
2-Thio-1,3-diphenylbenzalhydantoin,

 .—The condensation of thiodiphenylhydantoin with benzaldehyde was carried out as in the above cases. The product was purified by crystallizing from six parts of glacial acetic acid and then recrystallizing from 100 parts of alcohol. The alcoholic solution gave yellow needles melting to a clear, brown oil at 193°–194°. It was dried at 110° for analysis.

	Calculated for $C_{22}H_{16}ON_2S$.	Found. I.	II.	III.
C	74.16	73.48	....	....
H	4.49	4.14	....	....
N	7.87	....	7.78	7.86

This hydantoin was insoluble in cold alkali.

2-Thio-1,3-diphenylanisalhydantoin,



.—The mixture of thiodiphenylhydantoin, anisaldehyde, fused sodium acetate and glacial acetic acid, was heated somewhat longer than in the previous cases, as the condensation in this case appears to take place less readily. The product was difficultly soluble in glacial acetic acid, alcohol or acetone. From alcohol it formed poorly crystallized or indefinite granular masses. When crystallized from acetone it formed yellow needles which melted to a clear oil at 221°–222°.

	Calculated for $C_{23}H_{18}O_2N_2S$.	Found. I.	II.
N	7.25	7.05	7.11

New Haven, Conn.,
January, 1911.

[Contributions from the Kent Chemical Laboratory of the University of Chicago.]

ON THE ACTION OF NORMAL BARIUM HYDROXIDE ON *d*-GLUCOSE AND *d*-GALACTOSE.

By Fred W. Upson.

Kiliani[1] has maintained for some thirty years past that the formation of saccharinic acids, $C_6H_{12}O_6$, from the ordinary hexose sugars can be brought about only by the action of calcium hydroxide and that sodium, potassium and barium hydroxides do not lead to their formation. He ascribes, therefore, to the calcium a "specific" action. The work of Nef[2] on the action of alkaline hydroxides on the various hex-

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[1] Ber. d. chem. Ges., **15**, 2960; **26**, 1650; **35**, 3530.

[2] Ann. Chem. (Liebig), **357**, 303; **376**, 1–111.

oses and pentoses, as well as my own work, shows conclusively that the results are not to be interpreted on the basis of any such "specific" action. All alkaline hydroxides give entirely analogous results when the concentration conditions are similar, but the ratio of the various saccharinic acids formed varies remarkably with the concentration of the alkali used.

The following pages contain an account of an investigation, carried out by me at the suggestion and under the direction of Professor Nef, on the action of normal barium hydroxide on *d*-galactose and *d*-glucose. I succeeded in isolating some of the saccharinic acids (many of which are new compounds) which Nef[1] obtained by the action of 8 N sodium hydroxide upon these same sugars. A striking difference, however, was observed in the relative amounts of the various products obtained. Whereas Nef isolated considerable amounts of the α- and β-metasaccharinic acids of the *d*-glucose and *d*-galactose series and also α- and β-isosaccharin, I obtained in each case, by the action of the more dilute alkali, only very small amounts of the first three named, optically active C_6-saccharinic acids, as well as relatively large amounts of *d,l*-lactic acid and of *d,l*-1,3-dihydroxybutyric acid. The amount of optically inactive saccharinic acids, formed from synthetic pentoses and hexoses,[2] was also relatively larger in my experiments, which, of course, explains the greater difficulty in isolating completely the optically active compounds formed. The experimental work was carried out largely on the basis of the work of Nef just published in Liebig's *Annalen der Chemie*.

EXPERIMENTAL PART.

I. d-*Galactose and Normal Barium Hydroxide.*

A hot solution of 100 grams of *d*-galactose, melting at 155°–160°, in 250 cc. of water was added slowly, in the course of half an hour, with constant shaking to a filtered solution of barium hydroxide containing 400 grams of crystallized barium hydroxide in 2200 cc. of water and maintained at a temperature of 60°. The solution turned yellow at first and finally

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[1] Ann. Chem. (Liebig), **376**, 52–106.

[2] *Ibid.*, **376**, 9.

deep red-brown in color. After the addition of all of the sugar, the solution was at once placed in a large bath of boiling water and heated for eight hours, carbon dioxide, as well as air, being excluded by means of a condenser and receiver filled with water and connected with a soda-lime tube. No barium oxalate or carbonate was formed. The barium was removed by addition of the calculated amount of sulphuric acid and the precipitate filtered off and thoroughly washed. The combined filtrates were concentrated to about one liter by distillation under 20–30 mm. pressure and then treated so as to leave only a trace of barium in solution. On finally removing the water (under 25 mm., bath at 95°) a thick, dark brown gum remained. This was taken up in absolute alcohol and filtered from traces of barium salt. The weight of the nonvolatile saccharins, after complete removal of the alcohol, was 81 grams. These were resolved into two fractions by dissolving in 81 cc. of absolute alcohol and precipitating with twice this volume of ether. Only 4.6 grams of a gum, *D*, however, was deposited; the portion soluble in ether-alcohol amounted to 73.2 grams; it was dissolved in 100 cc. of water and extracted twenty times with about 150 cc. of ether each time. This effected a resolution into a portion remaining in the water, 37.5 grams, and into an ether-soluble portion, 31.6 grams. The 37.5 grams of gum remaining in the water was now further resolved, by solution in 37 cc. of alcohol and addition of 74 cc. of ether, into a fraction, *C*, 15.5 grams, insoluble in this mixture, and a soluble portion, 21.6 grams. The latter, dissolved in 20 cc. of water, gave, on twenty extractions with ether, 5.4 grams of ether-soluble gum, which was therefore united with the previous portion, 31.6 grams, mentioned above, giving a total of 37.0 grams crude C_3C_4-saccharinic acids (*A*), as a light, yellowish brown, mobile gum. The portion remaining in the water, 15.4 grams (*B*), as well as the above-mentioned fractions, (*C*), 15.5 grams, and (*D*), 4.6 grams, were all thick, very dark gums; it was therefore found necessary to remove the sugar tar present in these three fractions by acylation.[1] The acylation was

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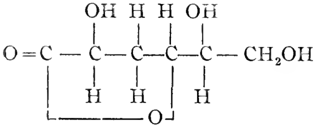
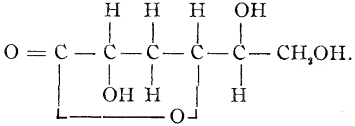
[1] Cf. Nef: Ann. Chem. (Liebig), **376**, 13–14.

carried out in the following manner: The gum was heated for nine hours at 100°–105° with three parts of acetic anhydride. The excess of acetic anhydride, as well as the acetic acid, were removed by distillation under 20 mm. pressure, the temperature of the bath being finally raised to 100°. The acylated gums were now separated from the insoluble tarry material by repeated extractions, first with cold and then with hot ether; they were then converted back into the free lactone gums, first by hydrolysis with five parts of water at 100°–110° for eight hours. After the removal of the water and acetic acid by distillation under 20 mm. pressure the gums were heated with 2 parts crystallized barium hydroxide and 2 parts water at 100° for eight hours. The barium was removed by precipitation with sulphuric acid and the water distilled off under 20 mm. pressure, a clear yellowish gum being left. All three fractions, (*B*), (*C*) and (*D*), mentioned above, were acylated in this manner; (*C*) and (*D*) were then united, giving 22.7 grams of acylated material soluble in ether and 5.7 grams of sugar tar. The former then gave, after complete hydrolysis, 13.2 grams light yellowish saccharins. Fraction (*B*) gave, on similar treatment, 21.7 grams acylated gums free from tar and then finally, on complete hydrolysis, 11.4 grams acid gums. The 13.2 grams of recovered saccharins mentioned above were resolved by digestion with 200 cc. of hot acetic ether into 11.6 grams of soluble gum and into 1.2 grams of insoluble material which was again acylated, yielding, finally, only 0.4 gram of saccharins free from tar. These, together with 1.5 grams of insoluble gum subsequently obtained from fraction (*A*) (see below), were now united with the 11.6 grams gum obtained from fraction (*B*). The total amount of saccharin free from tar thus obtained amounted, therefore, to 24.9 grams; these were now resolved, by digestion with a small amount of ether, into a soluble portion, I, 2.4 grams, and an insoluble portion, 19.6 grams. The latter was a thick, nonmobile, light yellow gum consisting mainly of C_5- and C_6-saccharinic acids, but still mixed with fairly large amounts of *d,l*-lactic acid and *d,l*-1,3-hydroxybutyrolactone. Accordingly, it was further resolved by digestion with acetic ether, ether, etc., into three fractions: I, 6.7 grams soluble in 800 cc. cold ether, which, united with 2.4 grams of a similar product just mentioned above, made a total of 9.1 grams gum, I (see below); II, 4.5 grams soluble in 60 cc. cold ethyl acetate; and III, 8.6 grams insoluble in the same amount of the last-named solvent. II and III were then worked up for *α*- and *β-d*-galactometasaccharins,



and



The separation of the various saccharinic acids was accomplished mainly by means of brucine; accordingly, it was first necessary to determine, by titration, the amount of alkaloid needed for the various fractions; this was invariably done as follows: An aliquot portion containing from 0.2 to 0.3 gram of lactone gum was treated with an excess of 0.1 N sodium hydroxide and heated for ten minutes on the boiling water bath. The end point was then determined by titrating back with 0.1 N hydrochloric acid and phenolphthalein as an indicator. Gum III, 8.6 grams, was therefore made up with water to 500 cc.; 15 cc. of this solution, corresponding to 0.258 gram, required 17.35 cc. 0.1 N alkali for neutralization, whereas 0.258 gram $C_6H_{10}O_5$ requires only 15.93 cc.; small amounts of the lower saccharinic acids or their lactones must therefore still have been present. Finally it was always found best by experience to subsequently treat the main portion of a titrated gum with 5 per cent. less brucine than the amount demanded theoretically on the basis of the titration. Accordingly, the main portion of gum III was digested with water and 20.5 grams of brucine for some hours on the boiling water bath, care being taken to heat one hour after complete solution of the alkaloid had taken place. The water was then removed by distillation at 50° under 10–20 mm. pressure; the 29.4 grams gummy brucine salts remaining gave, on crystallization from 50 cc. of 97 per cent. alcohol, 12.1 grams (in two crops) of crude *β-d*-galactometasaccharin brucine, melting from 105° to 120°. Fraction II, 4.5 grams, treated in a similar manner with 12.4 grams of brucine, etc., gave, besides 17.6 grams of gummy salts, only 1.65 grams of crystalline salts from alcohol, melting from 105°–120°. The combined unidentified gummy salts from II and III therefore amounted to 31.38 grams (see below). The total crude brucine salts of *β-d*-galactometasaccharin, 13.7 grams, melting at 105°–120°, recrystallized twice from three times their weight of 97 per cent. alcohol, yielded finally 6.0 grams of the pure salt melting at 137° to 138°.[1] This salt always crystallized rapidly from the above-named solvent in hard opaque nodules made up of masses of very fine needles. In order, however, to be absolutely sure of the purity of the final product the free lactone gum obtained from the purified brucine salt was first converted into the strychnine salt, etc. The salt was therefore digested in dilute aqueous solution with 1.5 times the required amount of aqueous barium hydroxide. The precipitated brucine was filtered off and well washed. The small amount of dissolved brucine was removed from the aqueous filtrate by fivefold extraction with benzene. The barium was then precipitated by means of sulphuric acid, the solution being finally left so that it still contained a trace of barium. The water was removed as usual by distillation *in vacuo* and the residual gum taken up in absolute alcohol and filtered from traces of barium salts, etc. This method was regularly used in recovering the acid gums from their brucine salts. The above-mentioned, practically pure brucine salt yielded in this way 1.6 grams of *β-d*-galactometasaccharin which, on long boiling with water and an excess of finely powdered strych-

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[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 304 and **376**, 75; also Killani: Ber. d. chem. Ges., **42**, 2609.

nine, gave 5.3 grams of crude strychnine salts. These, when crystallized from 12 cc. of 95 per cent. alcohol, gave 3.15 grams of voluminous, transparent, flat needles melting from 128° to 130° and possessing a specific rotation of $[\alpha]_D^{20} = -22°.95$; i. e., 0.7386 gram salt and 17.5686 grams water, therefore $p = 4.03$ and $d = 1.011$, gave in a 1 dcm. tube $[\alpha] = -0°.935$. These results agree very well with those recorded by Nef.[1] On setting free the gum from the strychnine salt in the usual way, 0.8966 gram of crude, almost colorless *β-d*-galactometasaccharin was obtained as a stiff gum which would not crystallize; it was identified by means of its specific rotation and then by conversion into its phenylhydrazide. Thus, 0.8966 gram lactone gum and 21.6435 grams water, therefore $p = 3.98$ and $d = 1.011$, gave in a 1 dcm. tube $[\alpha] = -2°.0$, whence $[\alpha]_D^{20} = -49°.67$.[2] The recovered gum was now converted into the phenylhydrazide by treatment at ordinary temperature with 0.9 cc. of phenylhydrazine and 0.9 cc. of absolute alcohol. The entire mass solidified spontaneously within a few hours through the formation of the hydrazide, but subsequently showed a tendency to become gummy when it was attempted to filter it. The hydrazide was found, therefore, in agreement with Nef's observations,[3] to be exceedingly unstable, but I finally succeeded in filtering off 0.85 gram of the substance in a crystalline condition; it was yellowish white in color, melted between 85° and 90° and gave the following results on analysis and optical investigation.

0.2047 gram dried *in vacuo* gave 0.3984 gram CO_2 and 0.1328 gram H_2O,

0.1987 gram substance gave 19.2 cc. dry N_2 at 21°.5 and 733.5 mm.

	Calculated for $C_{12}H_{18}O_5N_2$.	Found.
C	53.3	53.08
H	6.7	7.2
N	10.36	10.7

Optical rotation:

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[1] Cf. Nef: Ann. Chem. (Liebig), **376,** 76.

[2] Cf. Nef: *Ibid.*, **376,** 71, 76.

[3] Cf. Nef: *Ibid.*, **357,** 304; **376,** 78.

0.7842 gram phenylhydrazide and 18.8194 grams water, therefore $p = 4.0$, $d = 1.011$, gave in 1 dcm. tube $[\alpha] = —0°.08$; whence $[\alpha]_D^{20} = —1°.85$.[1] The formation of *β-d*-galactometasaccharin from galactose and normal barium hydroxide is therefore established beyond a doubt.

The total gummy brucine salts left from fractions II and III amounted, as stated above, to 31.38 grams; these gave back, on treatment with barium hydroxide, etc., 9.5 grams of acid gums which were resolved by digestion with 50 cc. of hot acetic ether into 3.8 grams soluble (*b*) and 5.7 grams insoluble (*c*) saccharins. The (*b*) fraction, when boiled with water and an excess of quinine for eight hours, gave 12.1 grams of crude quinine salts. On digesting with 20 cc. of absolute alcohol only 0.8 gram of crude *α-d*-isosaccharin quinine (see below), melting at 170°–190°, remained undissolved and 3.2 grams of saccharin gums (*b*) were recovered from the alcohol-soluble quinine salts, which were united with a similar gum obtained from fraction (*A*) (see below). The fraction (*c*), 5.7 grams, gave back, after acylation, 4.0 grams of clear, light-colored gum; on dissolving this in 4 cc. of absolute alcohol and scratching with a glass rod, 0.76 gram of crude *α-d*-galactometasaccharin crystals separated out without seeding; these melted from 138° to 142° and were therefore united with a similar product, 0.4 gram, obtained from fraction (*A*) (see page 468); the mother liquors still contained, therefore, 3 grams of noncrystallizable saccharins (*C*).

On crystallizing the 1.16 grams of crude *α-d*-galactometasaccharin from 8 cc. of absolute alcohol, 0.6 gram of the pure substance separated out in fine white, glistening plates, melting between 143° and 144°. Nef[2] records 144° as the melting point of *α-d*-galactometasaccharin, and Kiliani[3] 142°. The analysis and optical investigation of my product gave the following results:

0.1989 gram substance, dried *in vacuo*, gave 0.3227 gram CO_2 and 0.1135 gram H_2O.

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[1] Cf. Nef: Ann. Chem. (Liebig), **376**, 78.

[2] *Ibid.*, **357**, 304.

[3] Ber. d. chem. Ges., **16**, 2628.

	Calculated for $C_6H_{10}O_5$.	Found.
C	44.42	44.25
H	6.21	6.38

Optical rotation: 0.4272 gram α-metasaccharin and 9.3508 grams water, therefore $p = 4.36$ and $d = 1.011$, gave in a 1 dcm. tube $[\alpha] = -1°.89$, whence $[\alpha]_D^{20} = -42°.6$. The specific rotation of the substance is given as —48°.4 by Kiliani and as —45°.3 by Nef.[1] The identity of my product with *α-d*-galactometasaccharin was further confirmed by its conversion into the very characteristic phenylhydrazide. One and a quarter grams obtained from a previous experiment were dissolved in 1 cc. of water and 1 cc. of phenylhydrazine and 2 cc. of absolute alcohol were then added. After standing three days 1.65 grams of crude crystallized hydrazide separated out on the addition of ether. This compound, crystallized from 200 cc. of acetic ether, gave 1.3 grams of the pure product in white needles melting from 110°–112° and agreeing in all its properties with that described by Nef.[2] The analysis and optical investigation gave the following results:

Optical rotation: 0.5116 gram *α-d*-galactometasaccharin phenylhydrazide and 12.2000 grams water, therefore $p = 4.024$ and $d = 1.011$, gave in a 1 dcm. tube $[\alpha] = +1°.49$, whence $[\alpha]_D^{20} = +36°.6$. The specific rotation found by Nef[3] was +34°.38.

0.2100 gram substance dried *in vacuo* gave 0.4064 gram CO_2 and 0.1359 gram H_2O.

0.1802 gram substance gave 16.32 cc. dry nitrogen at 21° and 735.4 mm.

	Calculated for $C_{12}H_{18}O_5N_2$.	Found.
C	53.3	52.78
H	6.7	7.24
N	10.36	10.37

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[1] Ann. Chem. (Liebig), **376**, 72.

[2] *Ibid.*, **357**, 304. Cf. also Kiliani: Ber. d. chem. Ges., **42**, 2608.

[3] Ann. Chem. (Liebig), **376**, 73.

The C_3,C_4-Saccharinic Acids; d,l-*Lactic Acid*, $CH_3—\overset{*}{C}HOH—COOH$, *and* d,l-*1,3-Dihydroxybutyric Acid*, $CH_2OH—CH_2—\overset{*}{C}HOH—COOH$.

Fraction I, 9.1 grams (page 462) gum fairly soluble in cold ether, was made up to 500 cc. with water; 10 cc., equivalent to 0.186 gram gum, required 19.1 cc. of 0.1 N alkali for neutralization. The remainder was treated with 5 per cent. less than the theoretical amount of brucine in the usual manner; 44.7 grams of crude brucine salts were obtained which, on crystallization from absolute alcohol, gave a total of 20.5 grams of crystalline salts (in three crops). These melted from 170°–195° and must therefore have consisted mainly of brucine 1,3-dihydroxybutyrate. Twenty-five and one-tenth grams of gummy noncrystalline brucine salts remained in the filtrates (see below).

Fraction *A*, since it originally consisted of gums extracted from concentrated aqueous solutions by ether, obviously consisted mainly of *d,l*-lactic acid and 1-hydroxybutyrolactone. I found, in agreement with Nef, that it was impossible to separate these two substances by extraction from aqueous solution with ether—as is obvious from the following experiments: The gum (*A*), 37 grams, was dissolved in 144 cc. of water and extracted ten times with ether; 22.1 grams of gum were thus removed and these were then further resolved, by solution in four parts of water and tenfold extraction with ether, into 15.1 grams C_3,C_4-gums (I), soluble in ether, and 3.9 grams gum (*a*). The original aqueous solution, on tenfold further extraction with ether, gave 6.4 grams C_3,C_4-gums (II) and 9.8 grams gums still remained in the water solution; the latter, on digestion with 150 cc. ether, all dissolved except 1.5 grams referred to above (page 461). Therefore 8.3 grams of gum (*a′*) remained dissolved in this small amount of ether, which, with the 3.9 grams (*a*) just mentioned above, made a total of 12.2 grams mobile C_3,C_4-gums. The four fractions of C_3,C_4-gums (I), (II), (*a*) and (*a′*), were now treated separately with 5 per cent. less brucine than demanded on the basis of the titrations. On crystallizing the salts several times from absolute alcohol, from two to three crops of high-melting crystalline salts were obtained in every case. Those which melted above 200° and crystallized in cubes were united and worked up as *d,l*-lactic brucine, 41.5 grams;[1] while those melting from 175° to 190° and crystallizing in prisms, 82.5 grams, consisted mainly of *d,l*-1,3-dihydroxybutyric brucine. In all, only 28.1 grams of noncrystallizable brucine salts were finally found in the alcoholic mother liquors of the four fractions named above; these were therefore united with 25.1 grams of similar salts left from fraction I (page 467). Fourteen and seven-tenths grams of thick, very dark brown saccharin gums were obtained from these by the usual treatment with barium hydroxide, etc. On shaking these with 500 cc. cold ether 6 grams of C_3,C_4-gums dissolved. The insoluble portion, 7.6 grams, gave back, after acylation, etc., 3.9 grams saccharins free from tar. These were now united with 3 grams of unidentified gums (*C*) mentioned on page 465 and obtained from the alcoholic mother liquors of α-*d*-galactometasaccharin; also with gums (*b*), 3.2 grams, from which α-*d*-isosaccharin had been removed by treatment with quinine; and finally with 4.0 grams of stiff, difficultly soluble gums subsequently obtained from the combined crude 1,3-dihydroxybutyric salts, obviously mainly α- and β-isosaccharin. The total amount of these unidentified gums was therefore 13.7 grams. On digestion with 200 cc. of acetic ether, 7.0 grams of these gums dissolved, which were subsequently further resolved by ether, etc., into 3 grams of soluble and 4.0 grams of insoluble gums; the insoluble portion, 6.7 grams, gave back, after acylation, 4.7 grams of saccharins free from tar, which, on dissolving in a small amount of alcohol, etc., gave 0.4 gram crude α-*d*-galactometasaccharin crystals already referred to on page 465. The mother liquors were now united with the 4.0 grams left undissolved on digestion of the acetic ether extract, 7.0 grams, with ether, as stated above, and finally 7.3 grams of saccharin gums were recovered; these were made up to 500 cc. with water; 15 cc., corresponding to 0.219

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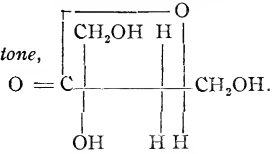
[1] Cf. Nef: Ann. Chem. (Liebig), **376**, 31.

gram gum, required 17.2 cc. 0.1 N alkali for neutralization. The main portion, treated with 21.06 grams of brucine, etc., gave 28.5 grams salts which on crystallization from alcohol gave 10.4 grams of crystalline brucine salts melting from 170° to 190°. These were therefore united with other salts of similar melting point. The gummy brucine salts, 17 grams, left in the alcoholic filtrate gave back 4.4 grams of saccharin gums which were boiled in water solution with an excess of quinine. On digesting the salts obtained, 16 grams, with absolute alcohol, 4.0 grams of crude *α-d*-isosaccharin quinine, melting at 195°–200°, remained undissolved. The alcohol-soluble quinine salts yielded 3.0 grams of nonmobile saccharin gum which was found to be optically inactive and was not further investigated.

α-d-*Isosaccharin*; *α-Hydroxymethyl*-l-*threo-1,4-dihydroxyvalerolactone,*



The 4.0 grams of crude isosaccharinic quinine was united with 0.8 gram of similar salt obtained from fraction (*b*) (page 465) and then digested with 15 cc. of absolute alcohol. The melting point of the insoluble salt, 2.1 grams, was 195° to 200°. It gave with barium hydroxide, etc., 0.6 gram of crude *α*-isosaccharin, which only partially solidified. It was therefore further purified by conversion into the very difficultly soluble calcium salt, 0.3 gram being obtained. From this 0.1 gram of *α-d*-isosaccharin was finally obtained in snow-white crystals melting at 94°. It is also certain from Nef's experiments that the *α-d*-isosaccharin present in a complex mixture of C_3-, C_4-, C_5-, and C_6-saccharins never can be separated out completely by means of the quinine salt and Dr. Nef informs me that he was always able to detect *α-d*-isosaccharin in such mixtures by means of the difficultly soluble mixed brucine salt of *α*- and *β-d*-isosaccharin[1] even

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[1] Ann. Chem. (Liebig), **376**, 57, 64.

when treatment with quinine had given no indication of its presence. This also explains why I was unable to find any α-*d*-isosaccharin in my experiments with *d*-glucose (see below). Finally, it should also be stated that I made no attempts to isolate the β-*d*-isosaccharin, also obviously present in my saccharin mixture, because this substance has not yet been isolated in a pure condition by Nef.[1]

The High-Melting Brucine Salts.

The total amount of crude 1,3-dihydroxybutyric brucine obtained from fractions I and II, (*a*) and (*a'*), was 82.5 grams, as stated above. These obviously still contained a fair amount of *d,l*-lactic acid, as well as α- and β-d-*isosaccharin.*[2] From this, 12.8 grams of crude 1-hydroxybutyrolactone was obtained by the usual treatment with barium hydroxide, but only 8.8 grams of this gum dissolved on shaking with 800 cc. of cold ether. The insoluble portion, 4.0 grams, which was dark and nonmobile and therefore consisted mainly of α- and β-*d*-isosaccharin, was now united, as already indicated on page 468, with other C_6-saccharin gums. The 8.8 grams of ether-soluble 1–hydroxybutyrolactone, including also 6.0 grams of ether-soluble C_3C_4-gums obtained from the gummy brucine salts (p. 468), were unfortunately united and then treated in the usual manner with 15 cc. each of phenylhydrazine and absolute alcohol. Contrary to expectations, no crystalline 1,3-dihydroxybutyric phenylhydrazide separated out. Nef has repeatedly observed that the presence of small amounts of other saccharins interferes greatly with the complete separation of 1,3-dihydroxybutyric phenylhydrazide. It is now obvious that the 1-hydroxybutyrolactone was contaminated with much lactic acid as well as C_6-isosaccharins. Accordingly, the gums, 14.0 grams, were recovered, after hydrolysis with barium hydroxide, etc.,[3] and again converted into the brucine salts. On crystallization from alcohol only 14.8 grams of crude 1,3-dihydroxybutyric brucine melting between 188° and 190° were obtained, and the salts left in

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[1] Ann. Chem. (Liebig), **376**, 56.

[2] *Ibid.*, **376**, 31, 63.

[3] Cf. *Ibid.*, **376**, 33.

the alcohol gave back 9.3 grams gum, only 3.1 grams of which were soluble in cold ether. The remainder, which was thick and dark, then gave, after acylation, etc., 2.4 grams of thick, optically inactive gum, which was not further investigated. The 3.1 grams of ether-soluble gum was united with 3.0 grams of similar gums obtained by extracting some crude C_6-gums with ether, as mentioned on page 468. The total gums, 5.9 grams, as found by accurate determination, were made up to 500 cc. with water and titrated in the usual manner; 20 cc., corresponding to 0.228 gram, required 20.4 cc. of 0.1 N alkali for neutralization. On treating the main portion with 5 per cent. less than the calculated amount of brucine, 18.48 grams, and crystallizing the crude salts from alcohol, 5.3 grams more of crude 1,3-dihydroxybutyric brucine melting at 188° was obtained. The gummy brucine salts, from which no more crystalline salts could be obtained, gave back 3.3 grams of thick saccharin gum, which was not further investigated.

The total amount of crude 1,3-dihydroxybutyric brucine,[1] melting from 188° to 190°, was 30.5 grams in three crops of 14.8, 5.3 and 10.4 grams; these yielded 5.6 grams of crude 1-hydroxybutyrolactone, soluble in cold ether; it was dissolved in 5.6 cc. of absolute alcohol and 5.6 cc. of phenylhydrazine added. The mixture solidified after several days and gave 3.2 grams of snow-white powdery *d,l*-1,3-dihydroxybutyric hydrazide on washing with acetic ether. The substance melted[2] between 129° and 130° and gave the following results on analysis:

0.1921 gram substance, dried *in vacuo*, gave 0.4010 gram CO_2 and 0.1240 gram H_2O.

0.2072 gram substance gave 24.7 cc. dry nitrogen at 22°.5 and 736.7 mm.

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[1] An optical investigation of a preparation of pure *d,l*-1,3-dihydroxybutyric brucine, obtained from the pure phenylhydrazide, and crystallizing in six-sided prisms, pointed at one end, and melting at 188° (cf. Nef: Ann. Chem. (Liebig), **376**, 31), gave the following results: 1.3458 grams salt and 31.7045 grams water, therefore $p = 4.05$, $d = 1.011$, gave in a 2 dcm. tube $[\alpha] = -2°.23$, whence $[\alpha]_D^{20} = -27°.23$.

[2] Cf. Nef: Ann. Chem. (Liebig), **376**, 33.

	Calculated for $C_{10}H_{14}O_3N_2$.	Found.
C	57.1	56.9
H	6.71	7.2
N	13.33	13.4

The total amount of crude *d,l*-lactic brucine[1] obtained, melting from 200° to 210°, was 41.5 grams, as mentioned above (page 468); this gave 8.6 grams of light-colored, mobile acid gum, which was heated in aqueous solution with excess of zinc carbonate for eight hours. The total amount of zinc lactate crystals obtained from the concentrated aqueous filtrate by addition of alcohol,[2] etc., was 7.1 grams, corresponding to 4.3 grams of free lactic acid. An analysis gave the following results:

2.0772 grams air-dried salt lost, on heating ten hours at 100° to 105°, 0.3768 gram H_2O.

0.2989 gram anhydrous salt gave, on ignition, 0.0993 gram ZnO.

	Calculated for $Zn(C_3H_5O_3)_2.3H_2O$.	Found.
H_2O	18.16	18.14
Zn	26.87	26.81

II. Dextrose and Normal Barium Hydroxide.

A hot solution of 100 grams *d*-glucose (melting at 145°–150°) was added slowly, in the course of half an hour, with constant shaking, to a filtered solution of 400 grams of crystallized barium hydroxide in 2000 cc. of water, maintained at a temperature of 60°. The mixture was then heated for five hours longer on a large bath of boiling water under the same conditions as described for *d*-galactose. No barium carbonate or barium oxalate was formed; the barium was removed as barium sulphate and the filtrates concentrated by distillation under 15 mm. pressure. The solution, containing finally only a trace of barium, was completely freed from water at the

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[1] Racemic lactic brucine, made from Kahlbaum's lactic acid and brucine, crystallizes from 4 parts of absolute alcohol in colorless transparent cubes, melting at 210°. The specific rotation of the salt was found to be —29°.05 (cf. Ann. Chem. (Liebig), **376**, 31), i. e., 1.1847 grams salt and 28.6327 gram water, therefore $d = 1.011$; $p = 3.97$, in a 2 dcm. tube gave $[\alpha] = -2°.33$.

[2] Cf. Nef: Ann. Chem. (Liebig), **335**, 270.

temperature of the boiling water bath. The gum was taken up in absolute alcohol, filtered from traces of barium salts and the alcohol removed by distillation *in vacuo*. There remained 80.2 grams of a dark brown, somewhat mobile gum. The gum was dissolved in 80 cc. of absolute alcohol and on addition of 160 cc. of ether 10 grams of dark tarry material were precipitated. On removal of the alcohol and ether from the soluble portion 70 grams of gum remained. This was resolved by several extractions with ether into a fraction (*A*), 51.4 grams of which was completely soluble in 500 cc. of cold ether, and an insoluble portion, 18.7 grams. The two insoluble portions were united (fraction *B*), 28.7 grams, and then acylated in the manner already described. There remained 10.6 grams of sugar tar, and 34.2 grams of ether-soluble acylated gums were obtained, which yielded, on subsequent hydrolysis, 17.2 grams of fairly thick, light colored gums (*B*).

Fraction (A), 51.4 Grams, Mainly d,l-*Lactic Acid and* d,l-*1-Hydroxybutyrolactone.*

Nef[1] has shown that the sugars of the *d*-glucose series give much larger amounts of lactic acid on treatment with alkalies than do the sugars of the *d*-galactose series. It was therefore possible to remove at once a large portion of the lactic acid present in fraction (*A*) by conversion into zinc salts, etc. The total amount of crystallized zinc *d,l*-lactate ($Zn(C_3H_5O_3)_2.3H_2O$), obtained in this way, was 41.6 grams, corresponding to 25.08 grams free lactic acid. The analysis of a portion of the zinc salt recrystallized from water gave the following results:

3.4277 grams air-dried salt lost, on heating for eight hours at 100°–105°, 0.6117 gram H_2O.

0.3985 gram anhydrous salt gave on ignition 0.1327 gram of ZnO.

	Calculated for $(C_3H_5O_3)_2Zn.3H_2O$.	Found.
H_2O	18.18	18.07
Zn	26.87	26.75

The aqueous alcoholic mother liquors from which, finally, no

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[1] Ann. Chem. (Liebig), **357**, 300, and **376**, 53.

more crystallized zinc lactate could be obtained, gave back with hydrogen sulphide, etc., 19.3 grams of gum. This was resolved by means of cold ether into a soluble portion, 13.6 grams, and an insoluble fraction, 5.9 grams. The ether-soluble portion, 13.6 grams, was made up to 1000 cc. with water, and 15 cc., equivalent to 0.203 gram, required 19.6 cc. 0.1 N alkali for neutralization. On treating the remainder as usual, with 48.6 grams brucine, etc., two crops, 27.0 grams, of crude 1,3-dihydroxybutyric brucine, melting from 188° to 190°, were obtained. To these were added 12.1 grams more of similar melting salts (2.2 + 9.9 grams) subsequently obtained from the second fraction (*B*) (see below). These then gave 8.3 grams of crude 1-hydroxybutyrolactone, which, on the usual treatment with 8 cc. each of phenylhydrazine and absolute alcohol, gave 5.3 grams of pure *d,l*-1,3-dihydroxybutyric phenylhydrazide, melting at 129°–130°.

0.1921 gram substance, dried *in vacuo*, gave 0.4010 gram CO_2 and 0.1240 gram H_2O.

0.2072 gram substance gave 24.7 cc. dry N_2 at 22°.5 and 736.7 mm.

	Calculated for $C_{10}H_{14}O_3N_2$.	Found.
C	57.1	56.9
H	6.71	7.2
N	13.33	13.4

The alcoholic mother liquors from the first two crops of 1,3-dihydroxybutyric brucine named above still contained about 35 grams of brucine salts; these gave in all 20 grams of low-melting (100°–120°) crystalline salts which are referred to later on. The noncrystallizable salts still left in the alcoholic filtrates gave back 3.2 grams of thick nonmobile saccharin gums, which were then treated as described below.

The above-mentioned saccharin gums, 5.9 grams, remaining undissolved in ether, were now resolved by means of 50 cc. of hot acetic ether into an insoluble portion, 1.4 grams, and a soluble fraction, 3.9 grams. The latter gave no crystalline salts on treatment with brucine or quinine and finally 3.3 grams of acid gums (*b*) were recovered. This fraction, as well as 1.4 grams insoluble gum, was then united with various other C_6-saccharin gums as described below.

When fraction (*B*), 17.2 grams, was boiled with water and an excess of finely powdered strychnine for ten hours, 60.2 grams of crude strychnine salts were obtained, but no crystalline salts were obtained by dissolving these in 60 cc. of alcohol. The saccharin gums were therefore again recovered, 16.8 grams, and resolved by digestion with much hot ether into 10.6 grams soluble gums and 6.2 grams insoluble saccharins. The latter was now united with 1.4 grams of a similar gum obtained, as already mentioned (p. 474), from fraction (*A*). Only 3.2 grams of saccharins free from tar were recovered from these after acylation, etc., which were now united with the 10.6 grams of ether-soluble gums mentioned above, 13.8 grams gum in all being thus obtained. On shaking these with 200 cc. of cold ether, 1.6 grams dissolved and gave with brucine, etc., 2.2 grams of 1,3-dihydroxybutyric brucine melting from 188° to 190°, which was therefore united with other salts of similar melting point, as already stated. The insoluble fraction, 12.2 grams, titrated too high for C_6-saccharins. It was made up to 500 cc. with water and 10 cc., equivalent to 0.22 gram gum, required 19.0 cc. of 0.1 N alkali for neutralization; obviously much 1-hydroxybutyrolactone was still present. On converting the remainder with 35 grams of brucine into salts and crystallizing these from alcohol, 9.9 grams more 1,3-dihydroxybutyric brucine, melting at 187°–190°, were obtained and therefore united with the corresponding salt, 27.1 grams, obtained from fraction (*A*), as already described above. There were also subsequently obtained 2.6 grams of a low-melting (100° to 120°) crystalline salt which was therefore united with 20 grams of similar salt obtained from fraction (*A*); these then gave, with barium hydroxide, etc., 4.2 grams of lactone gums. On boiling these with water and an excess of powdered strychnine and dissolving the 14.4 grams of crude salts thus obtained in 30 cc. alcohol, only 0.8 gram of crude β-dextrometasaccharinic brucine was obtained; the rest of the material then gave back 3.3 grams of lactone gum (*c*).

The gummy brucine salts still left in the alcoholic filtrates of fraction (*B*) similarly gave back 5.4 grams of lactone gum which were united with 3.2 grams of gum obtained from the noncrystalline brucine salts of fraction (*A*) and then boiled with water and an excess of powdered strychnine; on dissolving the 26.0 grams of crude salts thus obtained in 52 cc. of 95 per cent. alcohol, 3.7 grams of crude β-dextrometasaccharinic strychnine, decomposing between 178° and 185°, were obtained. These, together with the 0.8 gram similar salt mentioned above, gave back only 0.4 gram of β-dextrometasaccharin because of the presence of much free strychnine. The gummy strychnine salts left in the alcoholic filtrates similarly gave back 7.8 grams of free lactone gums; titration of a small portion of these at this point indicated the presence of C_3C_4-saccharins, which it seemed probable would interfere with the crystallization of the strychnine salts. This gum was therefore extracted several times with hot ether, 4.4 grams finally remaining undissolved. The ether extract was discarded. The 4.4 grams gum dissolved in water was then heated for four hours in an open dish on a boiling water bath in order to volatilize the 1-hydroxybutyrolactone and lactic acid still present. By this process the amount of the gum was reduced to 3.2 grams; it was now first treated with 7.8 grams of brucine and on crystallizing the 11 grams of crude salts obtained from 22 cc. of alcohol, 3.0 grams of crude β-dextrometasaccharin brucine, melting from 140° to 150° and possessing a specific rotation of —30°, were obtained. This shows that about 30 per cent. of the α-dextrometasaccharin salt was present.[1] The gum recovered from the salts still left in the alcoholic filtrates was not further investigated.

The 3.3 grams of gum (*c*) (p. 475) obtained from the noncrystalline strychnine salts was now united with fraction (*b*) (p. 474), 3.3 grams, and these were then diluted with water to 500 cc.; since 15 cc., corresponding to 0.198 gram gum, required 16.7 cc. 0.1 N alkali for neutralization, whereas 0.198 gram C_6-saccharin requires only 12.2 cc., some C_3,C_4-saccharinic acids must still have been present. The gum

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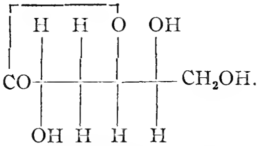
[1] Cf. Nef: Ann. Chem. (Liebig), **376**, 92.

was therefore dissolved in 12 cc. of water and extracted twenty times with ether. The 4.4 grams gum which remained in the aqueous solution was then heated with water in an open dish for four hours on the boiling water bath and thus finally 3.3 grams of gums free from C_3,C_4-saccharins were obtained. These were converted by means of 7.8 grams of brucine into salts and yielded on the first crystallization from 96 per cent. alcohol 1.6 grams of practically pure β-dextrometasaccharinic brucine melting between 145° and 150° and possessing a specific rotation of —33°. The 3.0 grams of saccharin gums recovered from the alcoholic mother liquors were found to have no effect on polarized light and were therefore not further investigated.

β-Dextrometasaccharin,



$$\mathrm{CO}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{O}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH}.$$

The total amount of crude β-dextrometasaccharinic brucine obtained in two lots (see above), was 4.6 grams; these yielded 0.8 gram of crude β-dextrometasaccharin gum which was then united with 0.4 gram of a similar gum obtained from the crude β-dextrometasaccharinic strychnine salts (p. 476). These were now boiled with water and an excess of powdered strychnine and finally gave, on crystallization of the salts obtained from alcohol, 2.1 grams of crude β-dextrometasaccharinic strychnine, melting with decomposition between 185° and 190°. This yielded 0.5 gram of crude β-dextrometasaccharin as a gum which would not crystallize. It was therefore converted into the calcium salt in the usual way and gave, on crystallization from concentrated aqueous solution by the addition of alcohol, 0.35 gram of white, heavy, crystalline needles of pure calcium β-dextrometasaccharinate. An optical investigation of the salt, dried *in vacuo* over sulphuric acid, gave the following result: 0.3545 gram calcium salt and 17.1648 grams water, therefore p = 2.03 and d = 1.010, gave in a 1 dcm. tube $[\alpha] = -0°.48$, whence $[\alpha]_D^{20} = -23°.41$. Nef[1] records $-23°.25$ as the specific rotation of this salt. The salt was now treated in aqueous solution with the theoretical amount of oxalic acid and the crude β-dextrometasaccharin then taken up in absolute alcohol and filtered from traces of calcium salt. A pure, almost colorless gum finally remained, which quickly solidified to a mass of fine, white, feathery crystals on seeding with a trace of the pure lactone; 0.12 gram of the substance, melting from 90° to 92°,[2] was obtained on washing well with acetic ether. An optical investigation gave the following results: 0.1264 gram β-dextrometasaccharin and 3.2068 grams water, therefore $p = 3.79$ and $d = 1.011$, gave in a 0.5 dcm. tube $[\alpha] = +0°.24$, whence $[\alpha]_D^{20} = +12°.53$. The result is somewhat higher than that recorded by Nef,[2] $+8°.2$, but is probably due to the small amount of material used in my determination. The gum recovered from the aqueous solution after making the optical observations was now treated with 0.1 cc. of phenylhydrazine and 0.2 cc. of absolute alcohol. The mixture solidified on standing overnight; 0.096 gram of the hydrazide was obtained in almost white, flaky crystals on filtering and washing with acetic ether; these melted from 125° to 130° and gave $[\alpha]_D^{20} = -29°.44$; i. e., 0.0962 gram hydrazide and 2.3673 grams water, therefore $p = 3.9$, $d = 1.011$, gave in a 0.25 dcm. tube $[\alpha] = -0°.29$, whence $[\alpha]_D^{20} = -29°.44$.[2] These results therefore establish beyond a doubt the formation of β-dextrometasaccharin from *d*-glucose and normal barium hydroxide.

I did not succeed in isolating any α-dextrometasaccharin or α- and β-*d*-isosaccharin in my experiments with *d*-glucose but these must obviously also have been present. It is clear that the presence of relatively larger amounts of optically inactive C_5- and C_6-saccharinic acids, formed from synthetic, optically inactive pentoses and hexoses, has made the detection and complete isolation of the optically active C_6-saccharinic acids present a problem of very unusual experimental difficulty.

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[1] Nef: Ann. Chem. (Liebig), **376**, 95.

[2] *Ibid.*, **376**, 96.

In conclusion the author would express sincere gratitude to Dr. Nef for his continued help and encouragement throughout the course of this work.

STUDIES IN ESTERIFICATION.

IV. THE INTERDEPENDENCE OF LIMITS AS EXEMPLIFIED IN THE TRANSFORMATION OF ESTERS.[1]

By E. Emmet Reid.

The classical experiments of Berthelot and Péan de St. Giles,[2] and the more exact work of Menschutkin[3] and Lichtz[4] have shown that when an organic acid is heated with an alcohol esterification takes place and a well-defined limit is reached, and that the same limit may be reached by heating the corresponding ester with water:

$$(1)\qquad CH_3COOH + HOC_2H_5 \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

In the case of acetic acid and ethyl alcohol, according to Menschutkin, if the acid and alcohol are present in equivalent amounts, equilibrium is reached when 66.57 per cent. of these have been transformed into ester and water. The same thing may be looked at in another way. It may be regarded as a case of partition and 66.57 and 33.43 be considered as partition factors. Then the acetyl, $CH_3CO.$, is partitioned between the $.OH$ and $.OC_2H_5$ groups. It is to be understood that it is not meant that such detached groups are present in the mixture. In this discussion no new theory of esterification is proposed and no one of the theories which have been put forth is favored or disfavored. The acid and alcohol may be written $CH_3COO.H$ and $HO.C_2H_5$ and the same equations set up in terms of these groups. Thus if $.OH$ and $.OC_2H_5$ groups are present in equal number, as in a mixture of equivalent amounts of acetic acid and alcohol, the relative amounts

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[1] This Journal, **41,** 483; **43,** 489; **45,** 38.

[2] Ann. chim. phys., [3] **65,** 385–422; **66,** 5–218; **68,** 225–359.

[3] Ber. d. chem. Ges., **10,** 1728; **11,** 1507.

[4] This Journal, **17,** 27; **18,** 590.

of acetyl combined with these two groups will be given in this form:

$$(2) \qquad \frac{CH_3CO.OC_2H_5}{CH_3CO.OH} = \frac{66.57}{33.43} = \frac{1.991}{1}$$

This number, 1.991, is the square root of k, the equilibrium constant given by the usual equation,

$$\frac{x^2}{(A-x)(B-x)} = k,$$

in which A and B are the original concentrations of acid and alcohol and x is the amount of ester at the limit. In case the acid and alcohol are not present in equivalent amounts, the actual amounts of $.OH$ and $.OC_2H_5$ present in the mixture, whether derived from $CH_3CO.OH$ or $H.OH$, or from $H.OC_2H_5$ or $CH_3CO.OC_2H_5$, are used in the calculation. Using the customary brackets to denote concentrations, we have at the limit:

$$(3) \frac{[CH_3CO.OC_2H_5]}{[CH_3CO.OH]} = \frac{[.OC_2H_5] \times 66.57}{[.OH] \times 33.43} = \frac{[.OC_2H_5] \times 1.991}{[.OH] \times 1}$$

In ordinary partition, such as that of a solute between two immiscible solvents, say iodine in ether and water, the solubility of the solute in the two solvents is more or less influenced by the fact that each solvent is somewhat altered by having dissolved some of the other solvent. The equilibria, particularly when several solutes and several solvents are present, are very complex, but in this, which we may call chemical partition, no such troubles arise. In the case of ester formation even such substances as hydrochloric acid, which enormously accelerate the approach to equilibrium, do not alter the location of the equilibrium point, or, in terms of the above, do not change the partition ratio 1.991 : 1. Acree[1] believes that catalysts which will change the equilibrium point may yet be found, but none have so far been reported, except, of course, those which form some sort of a combination with one or more of the reaction products. It is then not likely that the presence of some methyl alcohol

[1] This Journal, 38, 353.

would alter the above equilibrium between acetic acid and ethyl alcohol, that is, the partition of acetyl between hydroxyl and ethoxyl should not be affected by the presence of methoxyl, even though the methyl alcohol acts on its own account to produce some methyl acetate.

In the case of methyl alcohol, according to Menschutkin, if an equivalent amount of acetic acid is present, esterification reaches the limit at 69.52 per cent. of ester. Writing this in the form used above we have:

$$(4)\quad \frac{[CH_3CO.OCH_3]}{[CH_3CO.OH]} = \frac{[.OCH_3] \times 69.52}{[.OH] \times 30.43} = \frac{[.OCH_3] \times 2.281}{[.OH] \times 1}$$

If a quantity of acetic acid is heated with a mixture of methyl and ethyl alcohols, and if the presence of neither of the alcohols influences the equilibrium between the other alcohol and its ester, we will have at the limit:

$$[CH_3CO.OCH_3] : [CH_3CO.OC_2H_5] : [CH_3CO.OH] :: [.OCH_3] \times 2.281 : [.OC_2H_5] \times 1.991 : [.OH] \times 1.$$

Hence the amounts of methyl and ethyl esters present will be in the proportion

$$[CH_3CO.OCH_3] : [CH_3CO.OC_2H_5] :: [.OCH_3] \times 2.281 : [.OC_2H_5] \times 1.991.$$

Now, if under these same conditions, ethyl acetate is transformed directly into methyl acetate by methyl alcohol, and *vice versa*, according to the formulation:

$$(5)\quad CH_3CO.OC_2H_5 + HOCH_3 \rightleftarrows CH_3CO.OCH_3 + HOC_2H_5,$$

then the equilibrium, or partition, in this case will be represented by the equation

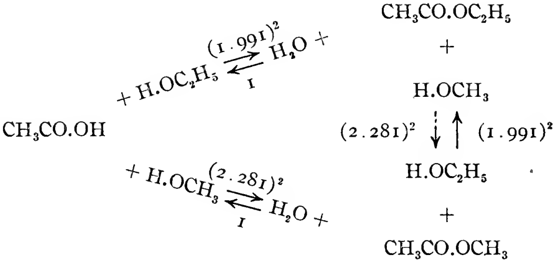
$$(5)\quad \frac{[CH_3CO.OCH_3]}{[CH_3CO.OC_2H_5]} = \frac{[.OCH_3] \times 2.281}{[.OC_2H_5] \times 1.991}.$$

This must be the case, else no equilibrium could be reached in the mixture, and there would be perpetual motion, a continuous transformation of acetic acid into one of the esters, this ester into the other ester and this back into the acid.

If we suppose that the esters in the above mixture are in equilibrium in the above ratio in presence of acetic acid it is difficult to see that this equilibrium between the two esters would be altered by the withdrawal of the acid. Hence we would expect that in case reaction (5) takes place between the esters and alcohols alone, that is, in the absence of acetic acid or of water, the same equilibrium point should be reached. That is, the partition of the acetyl between the methoxyl and ethoxyl is independent of other substances.

The three reactions involved may be represented in a triple formulation. The relative velocities of the reactions between equivalent quantities of the reacting substances are represented by numerals adjacent to the arrows, according to a notation introduced in a previous article.[1]

(7)



$$\begin{tikzcd}
 & H_2O + \begin{array}{c} CH_3CO.OC_2H_5 \\ + \\ H.OCH_3 \end{array} \arrow[dd, shift right, "(2.281)^2"'] \arrow[dl, shift left, "1"] \\
CH_3CO.OH \arrow[ur, shift left, "+H.OC_2H_5\quad (1.991)^2"] \arrow[dr, shift left, "+H.OCH_3\quad (2.281)^2"] & \\
 & H_2O + \begin{array}{c} H.OC_2H_5 \\ + \\ CH_3CO.OCH_3 \end{array} \arrow[uu, shift right, "(1.991)^2"'] \arrow[ul, shift left, "1"]
\end{tikzcd}$$

According to the above reasoning, when ethyl alcohol is heated with a methyl ester, and *vice versa*, the equilibrium point can be calculated from measurements made with the corresponding acid and the two alcohols, one at a time. Of course, the same reasoning may be expected to hold with other alcohols and their esters, as well as with mercaptans and their esters, and, possibly, also with amides, anilides, etc., in so far as other influences do not interfere.

Looking at esterification from the other side, it appears that the $.OC_2H_5$ group is partitioned between the H. and

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[1] THIS JOURNAL, **43**, 502.

CH_3CO. groups. According to this, if one acid acts on the ester of another acid, there should be equilibrium at a point which can be calculated from the esterification limits found by taking the two acids one at a time with the alcohol involved.

As, in inorganic chemistry, we have the partition of an acid between two bases and of a base between two acids, so in organic chemistry we must have the partition of an acid between two alcohols and of an alcohol between two acids. In both cases we may calculate the partition from other data, but as the experimental work below shows, this calculation is much simpler in the case of organic acids and alcohols. We may expect to find a volatile alcohol, or acid, being driven out by a nonvolatile alcohol or a nonvolatile acid. Finally, we may expect to find double decomposition between two esters such as ethyl acetate and methyl propionate, in which the acids and alcohols are different.

The limits found by Menschutkin[1] with acetic acid for the various alcohols are set down in Table I, and under these are put the partition factors calculated as above:

Table I.

	Methyl.	Ethyl.	Propyl.	*n*-Butyl.	Isobutyl.
Limit	69.52	66.57	66.85	67.30	67.38
Factor	2.231	1.991	2.016	2.058	0.266

	Octyl.	Cetyl.	Allyl.	Benzyl.	Styronyl.
Limit	72.34	80.39	59.41	60.75	64.58
Factor	2.615	4.099	1.464	1.548	1.820

In case a mixture of any number of these alcohols were heated with acetic acid, the amounts of the several esters formed and of the acid remaining free, when equilibrium is finally reached, may be calculated by multiplying the amount, expressed in equivalents, of each alcohol present by the proper factor from this table, summing up all these products, adding the amount of acid, also expressed in equivalents, multiplied by 1, and dividing the individual products by this sum. Thus, suppose 2 equivalents of methyl, 3 of ethyl, 3 of propyl and

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[1] Ber. d. chem. Ges., **10**, 1728; **11**, 1507.

2 of isobutyl alcohols to be heated with 5 equivalents of acetic acid, at equilibrium we should have a mixture of esters and free acid, the components of which are thus found to be $2 \times 2.281 + 3 \times 1.991 + 3 \times 2.016 + 2 \times 2.066 + 5 \times 1 = 25.715$. Then the amounts of the several esters, expressed in equivalents, will be

$$\frac{2 \times 2.281}{25.715}, \frac{3 \times 1.991}{25.715}, \frac{3 \times 1.016}{25.715} \text{ and } \frac{2 \times 2.066}{25.715},$$

and the amount of acid remaining will be

$$\frac{5 \times 1}{25.715}.$$

In Table II are given similar data for acids with ethyl alcohol, the limits being taken from the work of Berthelot and Péan de St. Giles,[1] Menschutkin[2] and Lichtz.[3]

Table II.

	Acetic.	Chlor-acetic.	Dichlor-acetic.	Trichlor-acetic.	Butyric.	Tartaric.	Succinic
Limit	66.57	68.65	71.22	74.00	70.2	66.6	66.0
Factor	1.991	2.190	2.475	2.846	2.356	1.995	1.941

	Valeric.	Stearic.	Pyro-tartaric.	Suberic.	Sebacic.	Citric.	Benzoic.
Limit	65.8	72.0	67.2	65.7	66.3	66.6	66.6
Factor	1.924	2.577	2.049	1.916	1.967	1.995	1.991

Equilibrium constants, from which limits may be calculated, for some aliphatic acids and a number of substituted benzoic acids are given in articles by Rosanoff and Prager[4] and by Prager.[5] Benzoic acid was studied by Berthelot and Péan de St. Giles,[6] who showed that it gave sensibly the same limit as acetic acid, 66.3 to 66.8 per cent., and hence the same equilibrium constant, approximately 4, instead of which Rosanoff and Prager find 0.4 (!), corresponding to a limit of about 38 per cent. esterification. They evidently did not

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[1] Ann. chim. phys., [3] **65**, 234; **66**, 5–128; **68**, 225.

[2] Ber. d. chem. Ges., **10**, 1728; **11**, 1507.

[3] THIS JOURNAL, **17**, 27; **13**, 590.

[4] J. Am. Chem. Soc., **30**, 1895.

[5] *Ibid.*, **30**, 1908.

[6] Ann. chim. phys., [3] **66**, 36, 52, 73, 101; **68**, 229, 267.

reach the limit on account of insufficient heating or else saponified some of the ester during titration. Since most of the acids with which they worked approached equilibrium much more slowly than benzoic acid, doubt is thrown on their other equilibrium constants, and as they used these in computing the reaction velocities, the latter are also open to question.

Unfortunately, we have data for the alcohols with only one acid and for the acids with only one alcohol, and hence have no means of knowing how an acid other than acetic would be partitioned between methyl and ethyl alcohols, but if such another acid, such as benzoic acid, is partitioned between hydroxyl and ethoxyl in the same ratio, i. e., has the same esterification limit as acetic acid, it is safe to assume that it will be partitioned between methoxyl and ethoxyl in the same ratio as is acetic; otherwise, this assumption is not safe. A comprehensive study of limits with a large number and variety of acids, each with a large variety of alcohols, is very desirable.

The question here considered, the interdependence of limits, is regarded as a general one, being nothing more than an application of the mass law and holding for reactions in inorganic as well as for those in organic chemistry, but it is here discussed in terms of the esters since they furnish a concrete example which is capable of experimental approach.

The question of the partition of an acid between two alcohols has been studied by the aid of the reciprocal transformations of the ethyl and methyl esters of benzoic acid, since these esters, being practically insoluble in water, are easily washed free from acid, and other impurities soluble in water, with little loss of the esters. The fact that their boiling points are far removed from those of water and of the corresponding alcohols also facilitates their purification. That they have so nearly the same boiling points, 199° and 212°, is also an advantage, since there is little danger of a change of composition of a mixture of the two esters on account of the evaporation of the more volatile constituent. The two esters differ sufficiently in density, 1.08714–1.04475, or 0.04239, to furnish an analytical method for the determination of the composition of a mixture of the two.

Since esterification limits may be determined far more accurately in the case of an acid such as acetic acid, which is readily soluble in water, the partition factors calculated above from the work of Menschutkin on acetic acid are assumed to hold for benzoic acid. Even if the partition factors are somewhat different for benzoic acid, their ratio cannot differ much from the ratio of those for acetic acid.

The question of the partition of an alcohol between two acids has been studied by the aid of the ethyl esters of benzoic and *p*-brombenzoic acids. These esters have the above-mentioned advantages of insolubility and high boiling points and a far greater difference in densities, 1.4385–1.0447, or 0.3938, so that 1 unit in the fourth decimal place corresponds to only 0.02 per cent. in the composition of a mixture of the two esters. This renders the density method even more accurate and permits the use of smaller samples of esters. The slight solubility of *p*-brombenzoic acid, 0.0037 gram in 100 cc. of water at 25°, about 15 times the solubility of barium sulphate, makes the washing of this acid out of a mixture of esters somewhat tedious, but is an advantage since it renders the testing of the completeness of the washing easy and certain.

One experiment has been tried on the replacement of acetic acid in benzyl benzoate, using the density method for the analysis of the resulting mixture.

Also a little work has been done on the question of double decomposition of two esters. For this, ethyl benzoate and benzyl acetate have been used since the boiling points of ethyl acetate, 77°, and that of benzyl benzoate, 323°, are sufficiently far removed from those of the other two esters, both of which boil near 212°, to render their separation possible.

The question of the partition of an acid between an oxygen and a sulphur alcohol has been studied in the transformation of ethyl benzoate into ethyl thiolbenzoate by mercaptan and of the thiol ester into the oxygen ester by alcohol. In this case the two esters chosen have the above-mentioned advantages of insolubility in water and high boiling points. The difference in density of the two esters is sufficient for the application of the density method of analysis, but on account of the difficulty of preparing considerable quantities of the thiol ester, the estimation of the sulphur content of the reaction product has been used instead.

In the partition of an acid between two alcohols some work has been done both with hydrochloric acid and with sodium alcoholates as catalysts, but since in the one case the equilibrium is disturbed by the unequally rapid action of the hydrochloric acid on the two alcohols to form alkyl chlorides, and in the other by the unequal distribution of the sodium between the two alcohols to form alcoholates, and by the formation of dense precipitates by the addition of even small percentages of sodium alcoholates to the esters, for accurate determinations of the partition factors, or equilibrium constants, recourse must be had to the experiments without catalysts Since, in the absence of any catalyst, even simple esterification proceeds very slowly at moderate temperatures, the transformation of esters, which may be regarded as the esterification of esters, may be expected to be a slow reaction unless accelerated by elevation of the temperature. Accordingly, for this part of the work, temperatures of from 200° to 230° have been used.

Partition of an Acid between Two Alcchols, or Ester Transformation.—A number of more or less isolated cases of the transformation of the ester of one alcohol into the ester of another alcohol are given in the literature, but it is difficult, if not impossible, to bring all of these together. In this line the classical work is that of Claisen in 1887.[1] He heated on the water bath benzyl benzoate with methyl alcohol and methyl benzoate with benzyl alcohol but got no reaction in either case. When he added sodium methylate to the former mixture and sodium benzylate to the latter, the mixtures solidified, and on acidifying with acetic acid transformation was found to have taken place. These transformations he assumed had taken place through the formation of the ortho compounds according to the scheme

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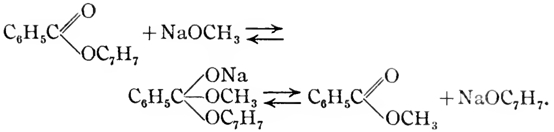
[1] Ber. d. chem. Ges., **20**, 646.

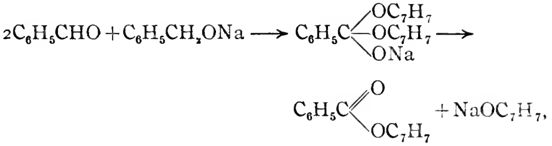
(8)



$$C_6H_5C\left\langle\begin{matrix}O\\OC_7H_7\end{matrix}\right. + NaOCH_3 \rightleftarrows C_6H_5C\left\langle\begin{matrix}ONa\\OCH_3\\OC_7H_7\end{matrix}\right. \rightleftarrows C_6H_5C\left\langle\begin{matrix}O\\OCH_3\end{matrix}\right. + NaOC_7H_7.$$

In the formation of benzyl benzoate from benzaldehyde, which he considered as taking place according to the formulation

(9)



$$2C_6H_5CHO + C_6H_5CH_2ONa \longrightarrow C_6H_5C\left\langle\begin{matrix}OC_7H_7\\OC_7H_7\\ONa\end{matrix}\right. \longrightarrow C_6H_5C\left\langle\begin{matrix}O\\OC_7H_7\end{matrix}\right. + NaOC_7H_7,$$

he noted that a small amount of sodium benzylate, since it is regenerated in the reaction, might transform an indefinite amount of the benzaldehyde.[1] His reasoning evidently applied equally well to the ester transformation, but he did not call attention to this.

Seelig,[2] in preparing benzyl acetate, heated benzyl chloride and potassium acetate in sealed tubes with ethyl alcohol. He noticed the formation of ethyl acetate and found that the higher he heated the mixture, the less benzyl acetate and the more benzyl alcohol he obtained. He supposed that the ethyl acetate was formed by the action of free acetic acid on the alcohol, but it is more likely that it was formed by the action of the ethyl alcohol at the temperature of 150°, at which he worked, on the benzyl acetate, giving ethyl acetate and benzyl alcohol.

Kossel and Kruger[3] showed that ethyl salicylate was formed from salol and sodium ethylate.

Henriques[4] studied the transformation of glycerides in alcoholic solution by sodium ethylate and showed that with as little as 15 per cent. of the alkali necessary for their saponifica-

[1] *Loc. cit.*, p. 650.

[2] J. prakt. Chem., [2] **39,** 157.

[3] Z. physiol. Chem., **15,** 321.

[4] Z. angew. Chem., **1898,** 338–345.

tion, the glycerides were completely transformed into the corresponding ethyl esters. He, as well as Kossel and Kruger, adopted the explanation of Claisen given above. The question of mechanism was further discussed by Goldschmidt.[1]

Shaklee[2] obtained benzyl acetacetate, almost quantitatively, by heating 20 grams benzyl alcohol and 40 grams ethyl acetacetate to 160°. Bacon[3] verified this, and prepared benzhydryl acetacetate by heating 50 grams benzhydrol with 100 grams ethyl acetacetate for 1 hour at 150°, the more volatile ethyl alcohol distilling over in both cases. These two experiments are of value in that they show that the reaction goes to completion in case one of the alcohols is volatile and cannot remain in the reacting mixture at the temperature used.

Much quantitative work on the transformation of esters, using sodium alcoholates as catalysts, has been done by Kremann[4] and Pfannl.[5] The former worked mainly with polyacetates, particularly triacetin, and finally came to the conclusion that a dynamic equilibrium exists in the sense of the formulation

$$(10)\quad C_3H_5(OOCCH_3)_3 + 3C_2H_5OH \underset{12.7}{\overset{1}{\rightleftarrows}} C_3H_5(OH)_3 + 3CH_3COOC_2H_5.$$

His analytical method was to distil the ethyl acetate off into an excess of standard alkali, the excess of which was subsequently titrated back. The nonvolatile triacetin remaining in the distillation flask was likewise determined by saponification. He found the backward velocity in the above reaction to be 12.7 times the forward velocity, the individual determinations running from 7.7 to 17.3. On treating a quantity of ethyl acetate with a large excess of glycerol and some alcoholic soda 20 per cent. of the ester was transformed into triacetin. With certain complex acids he considered the possibility of

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[1] Z. Elek. Chem., **10,** 221.

[2] Unpublished work quoted by Bacon and by Higley. THIS JOURNAL, **33,** 39; **37,** 310.

[3] THIS JOURNAL, **33,** 79.

[4] Monatsh., **26,** 783–822; **27,** 410–630; **29,** 23–44.

[5] *Ibid.*, **31,** 301 (1910).

steric hindrance to ester transformation. Sudborough[1] has shown that there is such hindrance in the case of doubly ortho-substituted acids.

Pfannl[2] showed that ester transformation is perfectly general, and that all of the reactions are reversible. He worked with the methyl, ethyl, and propyl esters of terephthalic, benzoic, and oxalic acids. He used "at least ten parts of the alcohol" to one part of the ester, which would mean 20 to 30 molecules of the alcohol to one of the ester. Since dimethyl terephthalate requires 100 parts of methyl alcohol for its solution, while the corresponding ethyl and propyl esters are very soluble in methyl alcohol, his method of work was to dissolve a quantity of the ethyl or propyl ester in 20 parts of methyl alcohol, adding the desired amount of sodium methylate, and note the time until crystals of the methyl ester began to appear. In this way he studied the influence of varying amounts of sodium methylate on the velocity of the reaction, showing that the velocity of the reaction is quite nearly proportional to the amount of alkali used. He adopted Claisen's view as to the mechanism of the reaction. "Without addition of alkali" he "could get absolutely no transformation, even when, to accelerate the reaction, the mixture was boiled two hours under a return condenser." When it is remembered that the mixture, consisting mainly of methyl alcohol, must have boiled at about 65°, this seems rather mild treatment, particularly as he had no test for small amounts of the methyl ester. In an experiment quoted below no crystals of a similar methyl ester were obtained, and hence no reaction detected, after heating for nearly 2 days at an average temperature of 165°. If the reaction velocity doubles for each 10° C., the velocity should be 1000 times as great at 165° as at 65°, hence Pfannl should have boiled his mixture about 2,000 days or over 5 years. It would be expected that the velocity of transformation of esters would be of the same order of magnitude as that of the formation of esters from the acids and alcohols, and it is well known how slow esterifica-

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[1] P. Chem. Soc., **21**, 87; through Chem. Centralbl., **1905**, I, 1234.

[2] *Loc. cit.*

tion is at moderate temperatures in the absence of a catalyst. By working from both ends he proved all the reactions reversible, but in all cases he used an enormous excess of the alcohol so as to get practically complete transformation, in one case actually isolating 92 per cent. of the calculated amount of ester. All of the products were carefully identified by physical properties and even by elementary analysis. In the case of methyl benzoate, which was transformed into the propyl ester by 19 molecules of propyl alcohol and 0.1 molecule of sodium propylate, 85 per cent. of the unsaponified ester was isolated as propyl benzoate. He made no attempts in any case to locate the equilibrium point.

Komnenos,[1] who does not refer to any of the above work, observed the transformation of the esters of acetylenetetracarboxylic acid by sodium alcoholates, and in order to determine whether it was due to the presence of $—CH_2—$ groups in which the hydrogen is replaceable by sodium, extended the study to esters of other acids, and finally to those of benzoic acid. He identified the esters obtained very thoroughly by elementary analysis, and by determining densities, melting points, etc., together with molecular weights and saponification equivalents. From 35 grams ethyl benzoate, 5.4 grams of sodium, and more than 180 grams of methyl alcohol he obtained 10 grams of crude ester, the largest portion of which distilled between 187° and 193° and which he considered as the "purest" methyl benzoate, though its density differed by 0.01 from the obsolete value which he quotes from Strohman.[2] The value which Komnenos did find is, however, only about 0.0015 low, which from Table III shows the presence of 3 per cent. of ethyl ester, which is just the amount which should have been present. He suggests that the reaction may proceed according to the mechanism above quoted from Claisen, though he does not seem to have been influenced by Claisen's work.

There are certain pseudoammonium bases which readily react with alcohols to form oxygen ethers, and which just as readily exchange one alcohol radical for another when simply

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[1] Monatsh., **31,** 111–122; **31,** 687–693; **32,** 77–88.

[2] J. prakt. Chem., [2] **36,** 4.

warmed in solution in excess of the second alcohol. These reactions are well discussed, with full references to the literature, by Johnson and Guest,[1] who also find that all the etherthioureas which they have prepared "react with alcohols, on warming, with transposition of the alkyl groups," the reactions being "reversible,

$$R.NHCSNHCH_2OC_2H_5 + CH_3OH \rightleftarrows R.NHCSNHCH_2OCH_3 + C_2H_5OH,$$

and . . . not influenced by the boiling points of the alcohols, or by the size of the alkyl groups involved in the change." It would be of interest to study quantitatively the equilibria involved and to extend this to the mercaptans.

In the present work encroachment on the fields of these workers has been avoided so far as possible and transformations have been affected by sodium alcoholates only far enough to show that the limits so obtained, making certain allowances for complications, are the same as those obtained without catalyst. It is hoped that these workers will continue their investigations and that the analytical methods here developed may prove serviceable to them.

Materials.

The ethyl alcohol used was very pure, about 99.995 per cent., having a density of 0.785108 at 25°, referred to water at the same temperature and reduced to a vacuum.[2]

The methyl alcohol had stood for a long time over anhydrous copper sulphate and was distilled from this. It had a density of 0.80018 (15°/15°). According to Doroszewski and Roshdestwenski[3] this corresponds to 98.623 per cent. of alcohol. Since the water content makes no difference and can be allowed for in the calculations, no attempt was made to dry it further.

The ethyl benzoate was a sample prepared for a previous investigation.[4] It was redistilled, as from long standing it had acquired a faint yellow color. Of this, 257 grams out of

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[1] J. Am. Chem. Soc., **32**, 1280.

[2] For this I am indebted to Dr. Robertson of this laboratory.

[3] Chem. Zentralbl., **1910**, I, 155.

[4] This Journal, **43**, 493.

300 distilled between 212°.2 and 212°.3, corrected. Practically all the rest went over within a fraction of a degree, but only the above-mentioned fraction was used in the quantitative work. The density was 1.04475 (25°/25°).

The methyl benzoate was prepared from the above sample of methyl alcohol. The crude ester was well washed with soda solution and then shaken ten times, for ten minutes each time, with more than its own volume of water. It was then dried for two weeks over fused calcium chloride. On distillation, 230 grams out of 313 went over between 198°.8 and 199°.1, most of the remainder going over within a degree. The largest portion boiled at 198°.9 at 753.9 mm. (thermometer stem in the vapor). It had a density of 1.08714 (25°/25°), uncorrected for air displacement.

The ethyl *p*-brombenzoate was prepared from acid melting at 249°.5 (uncor.), or 1°.5 below the best acid. It was well washed and dried by passing hydrogen through it at 100°. On distillation, 16.6 grams of it distilled from 264° to 267°, leaving about 1 gram residue. Of the first fraction, on redistillation, 15 grams went over from 264° to 267°. Nearly all of this went over between 265°.5 and 266°.5 at 768.1 mm., the stem of the thermometer being entirely in the vapor. Errera[1] gives 262° (cor.) at 737 mm. The 264°–267° fraction alone was used in the quantitative work. Its density was 1.43537 (25°/25°), not corrected for air displacement. The Anschütz thermometer used gave the boiling point of acetanilide as 305°, agreeing exactly with Perkin's determination.

The benzyl acetate used was prepared according to the method of Seelig.[2] The crude ester was washed twice with soda solution and twice with water. On distilling, 5 grams went over up to 213°, 133 grams between 213° and 217°, and 9 grams from 217° to 218°, leaving 3 grams of residue. The second fraction was redistilled; 19 grams went over below 214°, and 90 grams from 214° to 216°, leaving 16 grams residue. Most of this 90 grams boiled very close to 215°.3 at

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[1] Gazz. chim. ital., **17,** 211.

[2] J. prakt. Chem., [2] **39,** 162.

756.6 mm. An Anschütz thermometer was used and the stem was entirely in the vapor. This boiling point is considerably above 206°, the boiling point given by Conrad and Hodgkinson,[1] but not so much above the 210° to 213° mentioned by Higley.[2] The fraction between 214° and 216° had a density of 1.05462 (25°/25°). Only this was used in the quantitative work.

The ethyl thiolbenzoate was the same sample used in a previous investigation.[3]

The mercaptan was also a part of the preparation previously used.[3]

Preliminary Experiments.

With Hydrochloric Acid as Catalyst.—To 1.200 grams of ethyl *p*-brombenzoate (4.240 millimoles) was added 4.921 grams of methyl alcohol (152 millimoles), and dry hydrochloric acid passed in to the amount of 0.163 gram, or about 3 per cent. of the weight of the alcohol. The mixture was then sealed up and heated in a boiling water bath for 1.5 hours. On cooling the mixture, beautiful white needles separated. No pressure was found when the tube was opened. On evaporation the mixture left 1.1123 grams of white needles, the calculated weight of methyl ester being 1.125 grams. These melted without purification at 68° to 71° and after crystallizing once from methyl alcohol at 78°. The melting point of methyl *p*-brombenzoate is given by Rupe[4] as 81°, by Sudborough[5] as 78°, and by Thiele and Rossner[6] as 79°–80°.

This experiment shows in a clear-cut way that the ester of one alcohol can be transformed into the ester of another alcohol under the influence of hydrochloric acid. That is, ethyl *p*-brombenzoate may be esterified by methyl alcohol, and a methyl ester produced, under exactly the same conditions under which the free acid is esterified. The low melting point of the crude product indicates that a small amount of the ethyl ester remained.

[1] Ann. Chem. (Liebig), **193**, 320.
[2] This Journal, **37**, 311.
[3] *Loc. cit.*
[4] Ber. d. chem. Ges., **28**, 260.
[5] J. Chem. Soc., **67**, 592.
[6] Ann. Chem. (Liebig), **306**, 212.

Without Catalyst.—A mixture of 0.4819 gram ethyl *p*-brombenzoate and 2.1915 grams methyl alcohol was sealed up and heated 24 hours at about 150° and then 20 hours at about 180°. Since, on cooling the mixture below 0°, no crystals were formed, it was further heated for 42 hours at about 208°–215°. This time, on cooling to —20°, an abundance of white needles formed. On remaining a long time at room temperature, the fine needles were transformed into large transparent flat needles. Slight pressure was found on opening the tube. The needles, after simply wiping with filter paper, melted at 78°.4.

This experiment shows that the transformation of an ester of one alcohol into the ester of another alcohol, or the esterification of an ester, takes place, without catalyst, under the same conditions, at something like the same rate as the esterification of the corresponding acid.

The Partition of Benzoic Acid between Ethyl and Methyl Alcohols.

Analytical Method.—Since ethyl benzoate has an apparent density of 1.04475 (25°/25°) and methyl benzoate a density of 1.08712 (25°/25°) the difference in density is 0.04237. Hence, provided there were no contraction or expansion on mixing, 1 part of methyl benzoate added to 424 parts of the ethyl ester would raise the density by one unit in the fourth decimal place, which means that in a mixture of the two a difference of density of 0.0001 corresponds to a difference of 0.23 per cent. in the composition of the mixture. In order to ascertain the change of volume on mixing the two esters, five mixtures of varying proportions were made up and the densities of these taken.

The next question was whether a method of treatment could be found which would certainly free the mixture of esters from benzoic acid, water, ethyl and methyl alcohols without altering the relative proportion of the two esters in the mixture. After taking the densities of the above-mentioned five mixtures, each of which weighed about 12 grams, 4 cc. of ethyl and 2 cc. of methyl alcohol, together with about 0.2 gram benzoic acid, were added to each and then each put through the following purification process. The mixture was put into a tube about 13 × 320 mm. closed at one end. An approximately equal volume of 2 per cent. sodium bicarbonate solution was added, the tube corked and shaken for ten minutes. The aqueous portion was pipetted off, and the ester mixture further washed three times with at least its own volume of water, the shaking being continued ten minutes each time. After the last washing the mixture was poured into a test tube and as much as possible of the water removed by wiping with damp filter paper. The tube was then placed in a bath of boiling water for one hour, a current of dry hydrogen, issuing from a fine capillary, being passed through the mixture. The density was then taken. In Table III are given in the first line the original molecular percentages, next the weight percentages, then the original density, the difference in density corresponding to 1 molecular per cent. of methyl ester, and lastly the density after the above treatment, and the error in molecular per cent. of methyl ester.

Table III.

	I.	II.	III.	IV.	V.	VI.	VII.
Mol. per cent. methyl ester	0.00	19.95	38.08	49.00	68.59	79.14	100.0
Wt. per cent. methyl ester	0.00	18.43	35.80	46.55	61.29	77.47	100.0
Density	1.04475	1.05231	1.05949	1.06404	1.07047	1.07739	1.08714
Difference for 1 per cent.	.....	0.000379	0.000396	0.000417	0.000441	0.000445	0.000467
Density found	.....	1.05238	1.05944	1.06414	1.07037	1.07138	......
Error in per cent. of ester	.....	0.14	0.12	0.23	0.23	0.02	......

The densities were taken with pycnometers such as described by Jones and Bingham.[1] A number of these were used, varying in capacity from 8 to 1.3 cc., according to the amount of liquid available. With the larger ones 0.1 mg. difference in the weight of the filled pycnometer corresponds to a difference of 0.00001 in the density while in the smallest the same difference in weight corresponds to 0.0001 in the density. For uniformity all of the densities are carried out to five places of decimals, but little importance is attached to the last figure. In the analyses, in the experiments which follow, the percentages reported were found by interpolation from the above table, the molecular percentage being supposed to increase regularly as the density between the two points determined. Since the curve joining the points is not a straight line, this is not strictly correct, but the error thus made is not great.

The data as to densities of the mixture in the above table are presented in the diagram, Fig. I. Since all the points representing the densities of mixtures lie below the straight line which is drawn joining the densities of the pure esters, the densities of all mixtures are less than the average densi-

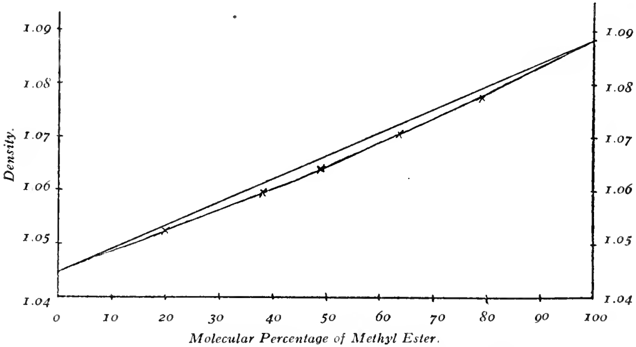

Figure I.—Densities of Mixtures of Ethyl and Methyl Benzoates.

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[1] This Journal, **34,** 495.

ties of the components, and hence there is expansion on mixing.

All of the densities were taken at 25° and compared with water at the same temperature. No correction was made for air displacement. As the densities are all nearly the same and also not far from that of water this correction would be very small. Before setting, each pycnometer was allowed to remain in a large water bath, the temperature of which seldom varied more than several thousandths of a degree from the mean temperature.[1] On account of the high viscosity of the esters they do not drain properly and a considerable amount of liquid always sticks to the sides of the small bulb in the pycnometer. This is probably much the largest source of error in the determinations. The magnitude of the error due to this was not realized in the first part of the work, but in the latter part this error was minimized by taking care that in filling the pycnometer the liquid was either not drawn into the bulb at all or only a very little of the way in. This was accomplished by putting a Mohr pinchcock on the rubber tube through which air was drawn to cause the liquid to rise in the pycnometer. This was closed when the liquid had risen just a little way above the mark. The pinchcock remained on the pycnometer all the time it was in the bath, and the final setting was made by squeezing the rubber tube between the pycnometer and the pinchcock. Each time, before use, a pycnometer was rinsed out four times with alcohol and dried by warming and aspirating air through it. When taken out of the bath the pycnometers were rinsed off with alcohol, wiped with bibulous paper, and allowed to stand in the balance case for a considerable time, usually a half hour, before weighing.

Experiments with Hydrochloric Acid as Catalyst.—Two mixtures of methyl benzoate and ethyl alcohol and one of ethyl ester and methyl alcohol were made up and dry hydrochloric acid passed in for ten minutes, the mixture being kept at 0°. The mixtures were sealed up and kept at 75°

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[1] For the use of this excellently regulated bath I am indebted to the kindness of Associate Professor Acree.

for 3 hours and then at 85° for 8.5 hours. Before being put through the regular process described above, the mixtures were given a preliminary washing with water to remove most of the hydrochloric acid. In all of the reaction mixtures considerable amounts of alkyl chlorides appeared to be present, as gas was given off continuously during the washing. The proportions of the constituents, as well as the results obtained, are given below in Table IV, in which the actual weights are given in the first three lines, and the weights in millimoles in the next three:

Table IV.

	Methyl ester and ethyl alcohol.		Ethyl ester and methyl alcohol.
Weight of ester	11.173	11.145	12.016
Weight of alcohol	4.704	9.597	3.011
Weight of HCl	2.206	2.421	2.214
Ester in millimoles	82.12	81.92	80.06
Alcohol in millimoles	102.15	208.4	92.77
HCl in millimoles	50.52	66.42	62.16
Density of product	1.05980	1.05436	1.06266
Per cent. of methyl ester, found	38.82	25.12	45.69
Per cent. of methyl ester, calculated	47.92	31.04	57.00

Under "calculated" is put the per cent. obtained by multiplying the equivalent amount of methyl, whether originally present in the ester or in the alcohol, by 1.145, the equivalent amount of ethyl present by 1, and calculating the percentages with these two numbers. This is the same as assuming that the benzoyl is partitioned between methoxyl and ethoxyl, when present in equivalent amounts, in the ratio of 2.281 to 1.991. These three experiments confirm the one given above in showing that ester transformation takes place readily in the presence of hydrochloric acid, and further that the reaction proceeds readily from either end, even when large excesses of the alcohols are not used. The percentages of the two esters found do not agree with the calculated equilibrium points, there being in all cases less of the methyl ester than was expected. The deficiency is greatest when there was least of the methyl alcohol and least when there was the most of that alcohol. This is readily accounted for by supposing that the hydrochloric acid acted to a greater extent on the methyl than on the ethyl alcohol to form alkyl chlorides.

The following experiments were made, using only about one-tenth as large a proportion of hydrochloric acid and a much lower temperature. The samples were made up and sealed up in exactly the same way as the above except that the hydrochloric acid was passed for only 30 seconds and, after sealing, the tubes were put in the 25° thermostat. On account of the smaller amounts of ester mixture a 3-gram pycnometer was used. The last sample remained at 25° for about 71 hours, the other three for 28 days. The results are given in Table V in the usual form:

Table V.

	Ethyl ester and methyl alcohol.		Methyl ester and ethyl alcohol.	
Weight of ester	5.0940	5.0620	5.2432	5.4147
Weight of alcohol	4.0066	1.5793	1.3495	5.0527
Weight of acid	0.1110	0.1148	0.1606	0.1080
Ester in millimoles	33.94	33.73	38.54	39.80
Alcohol in millimoles	124.69	49.15	29.30	109.72
Hydrochloric acid in millimoles	3.045	3.150	4.406	2.963
Density of product	1.07754	1.0	1.06477	1.08090
Per cent. of methyl ester, found	79.59	65.09	50.66	86.42
Per cent. of methyl ester, calculated	80.60	64.92	60.00	29.34

The results here given show the same things as those in Table IV and the deficiency of methyl ester, which is less in this case, may be explained in the same way. The fourth sample, which was heated only 71 hours at 25°, shows something of the rate of the reaction.

With Sodium Alcoholates as Catalysts.—The following eight experiments were made to determine the equilibrium point, using sodium alcoholates to accelerate the reactions. In the first set of four, for 1 molecule of ester from 0.02 to 0.03 molecule of the alcoholate was used, and in the second set, 0.01 or less. In each experiment the ester and alcohol were successively weighed into a test tube which had previously been drawn down to a narrow neck. A bit of freshly-cut sodium was dipped in alcohol, then in ether, quickly wiped off, and thrown into the tube. As soon as the evolution of hydrogen had ceased the tube was sealed off and weighed. The gain in weight was multiplied by 23/22 to obtain the weight of the sodium. The first four samples remained at room temperature for 14 days and the others for 15 days. Of the first set, the first mixture remained perfectly clear and colorless, while in the second a precipitate began to form soon after adding the sodium and increased in amount during the first day or two till the whole mixture solidified entirely to a pure white, cheesy mass from which not a drop of liquid could be separated even by vigorous shaking. In the third mixture the precipitate soon began to form and continued till it filled much of the solution, but considerable clear liquid remained. The fourth mixture remained clear for quite a time, but finally deposited a small amount of precipitate, a part of which was granular and the rest gelatinous. The precipitates in the last two did not resemble that in the second tube, but were more gelatinous and semitransparent, somewhat like freshly precipitated silicic acid. Both of these turned slightly yellow. Such precipitates have been noticed by Claisen, Higley, Komnenos, and others. The analytical process was identical with that above described except that the mixtures were given a preliminary wash, with only slight shaking, with the sodium bicarbonate solution so as to eliminate the caustic alkali. The results of the first set are given in the usual form in Table VI:

Table VI.

	Ethyl ester and methyl alcohol.		Methyl ester and ethyl alcohol.	
Weight of ester	5.1914	5.3798	5.2788	5.5584
Weight of alcohol	7.1302	1.6945	2.1612	7.8359
Weight of sodium	0.0161	0.0275	0.0282	0.0225
Ester in millimoles	34.59	35.85	38.80	40.85
Alcohol in millimoles	219.68	52.21	46.93	170.16
Sodium in millimoles	0.698	1.193	1.225	0.976
Density found	1.08183	1.07063	1.06421	1.05411
Per cent. of methyl ester, found	88.49	63.95	49.41	24.50
Per cent. of methyl ester, calculated	87.91	62.51	48.74	21.56
Difference	0.58	1.44	0.67	2.94

Of the second set of four experiments, the first mixture remained perfectly clear and colorless, in the second a precipitate formed and took up most of the solution, and in the third after some time a gelatinous precipitate appeared, while in the last there was nothing for quite a while, but finally a partly granular and partly gelatinous precipitate. The third and fourth turned slightly yellow. In the third mixture the ester and alcohol were almost exactly equivalent and the sodium alkylate just 1 per cent. of the alcohol. The results are given in the usual way in Table VII:

Table VII.

	Ethyl ester and methyl alcohol.		Methyl ester and ethyl alcohol.	
Weight of ester	5.3963	5.3251	4.9089	5.2051
Weight of alcohol	3.3777	1.7122	1.6731	3.2184
Weight of sodium	0.0071	0.0085	0.0084	0.0078
Ester in millimoles	35.96	35.48	36.08	38.26
Alcohol in millimoles	104.07	52.75	36.33	69.89
Sodium in millimoles	0.308	0.366	0.363	0.340
Density found	1.07741	1.07083	1.06664	1.05949
Per cent. of methyl ester, found	79.10	64.40	54.89	39.78
Per cent. of methyl ester, calculated	76.82	63.00	53.21	38.53
Difference	2.28	1.40	1.67	1.25

It will be noted that, of these eight experiments, four begin with methyl and four with ethyl ester. In two with each ester a large excess of the alcohol was used so as to transform the major portion of the ester. In the first experiment of the first set over 88 per cent. of the original ethyl ester was transformed into the methyl ester, while in the fourth experiment of the same set, over 78 per cent. of the original methyl ester was transformed into the ethyl ester. In all the experiments excess of the alcohol was used. In case of the methyl alcohol the equivalents given are those of the alcohol actually present, making deduction for the water content of the sample.

It will be seen that the results obtained corroborate the observations of all the workers above quoted in that they prove that the transformations take place readily at ordinary temperatures under the influence of even small amounts of the alcoholates and that all of the reactions are readily reversible. It is seen, however, that the enormous excess of the alcohols, 10 to 30 equivalents to one of ester, which have been commonly used, are by no means essential to demonstrate the fact of transformation, though, of course, if it is desired to make the transformation practically complete, such proportions are required in order to reduce the original ester to a negligible impurity.

The results obtained approximate quite closely the figures calculated on the assumption that the partition of the benzoyl between the methoxyl and ethoxyl is according to the partition factors calculated above, and the general proposition may be regarded as proved for this case and rendered probable for other cases, though the differences between "found" and "calculated" are greater than the probable errors with the 3-gram pycnometer used It is difficult to see how equilibrium can be reached in mixtures apparently so far from homogeneous as these were, but, owing to the smallness of the total amount of sodium present, the precipitates observed in the above described mixtures, though exceedingly bulky in appearance, must in reality have been small in actual amount, and must, at any one time, have involved only a small proportion of the reacting substances. Since the amounts, and hence the ratios, of the free alcohols and free esters are altered by a withdrawal of a portion of each of them to form the intermediate product, if a sensible amount of such intermediate product is formed and remains, the equilibrium may thereby be sensibly altered. From the work of Lobry de Bruyn[1] it appears that if, say 17 molecules of sodium were added to a mixture containing 100 molecules each of methyl and ethyl alcohols, there would result 15 molecules of sodium methylate and 2 molecules of the ethylate, leaving the ratio of the alcohols as 85 : 98, which is considerably different from the original ratio 100 : 100. Hence any catalytic agent which forms complexes with any sensible amounts of the reacting substances may be expected to alter the equilibrium. This is different from the supposition made by Acree[2] that a catalyst may be found which will accelerate the forward reaction according to the mth power and the reverse reaction according to the nth power of its concentration. In their discussions, Stieglitz, Acree and others have always postulated that a small amount of the intermediate product should be formed. It appears, then, that for accurate determinations of equilibria, the use of a catalyst is to be avoided as far as possible.

In the case of the esters of acetylenetetracarboxylic acid, Komnenos[3] found that "it is noteworthy that ethyl replaces methyl more readily than the reverse." This statement, for which he offers no sort of quantitative evidence, is rendered improbable by the present experiments.

It is to be noted that in all eight experiments the proportions of methyl ester found are in excess of the amounts calculated. In case the factor, 1.145, which was used in the above calculations, were too small, an excess of methyl ester should also have been found, but in this case the excess would have been proportional to the amount of methoxyl present. This is not found to be the case. It was thought that the excess of methyl ester might have been only apparent, the

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[1] Rec. trav. chim., **18,** 41–71 (1899).

[2] This Journal, **38,** 353.

[3] Monatsh., **31,** 121.

excess of density of about 0.001 being due to small amounts of one or more complex substances formed by the action of the sodium alcoholates on the esters. Such substances were found by Higley[1] under somewhat similar conditions. To test this supposition, about 10 milligrams of sodium was added to a mixture of 5 cc. each of ethyl alcohol and ethyl benzoate. This mixture was sealed up and kept at room temperature for 9 days, when it was put through the usual analytical process. In a 3-gram pycnometer, the resulting ester showed the density of 1.04470 as compared with 1.04475 for the original ester. From this it may be concluded that the excess of density found above was not due to the formation of complex compounds.

Velocity of the Reaction with Sodium Alcoholates.—In order to obtain some idea as to the rate of change, under the influence of these catalysts, the following two experiments were made with methyl benzoate and ethyl alcohol at 25°. The times given are only approximate as, in each case, about five minutes was required for the solution of the sodium and the sealing of the tube, and several minutes more for the weighing, though no great amount of transformation could have taken place during this time, as care was taken not to shake the tube and the light alcohol layer remained quite distinct from the heavy ester on which it floated. On putting into the 25° bath, mixing was effected by shaking and the time counted from this moment. The reaction was stopped by pouring the mixture into the sodium bicarbonate solution acidified with an amount of acid equivalent to the amount of sodium alcoholate present. It appears that in 200 minutes the reaction is practically complete, while in the 20-minute experiment only 78.3 per cent. of the possible transformation had taken place. The data are given in the usual form in Table VIII:

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[1] THIS JOURNAL, **37**, 311.

Table VIII.

Time in minutes	200.0	20.0
Ester in grams	5.5341	5.1936
Alcohol in grams	6.1215	6.5342
Sodium in grams	0.0110	0.0184
Ester in millimoles	40.68	38.17
Alcohol in millimoles	132.93	141.89
Sodium in millimoles	0.476	0.798
Density of product	1.05570	1.05635
Per cent. methyl ester, found	28.45	30.07
Per cent. methyl ester, calculated	25.94	23.55

Assuming, for a rough calculation, that the alcohol remains constant during the reaction, we find that 7.4 per cent. of the ester is transformed per minute by 2.1 per cent. of the sodium ethylate equivalent to the ester present. In the experiment given above in Table V, in which methyl benzoate was transformed by 7.4 per cent. of its own equivalent of hydrochloric acid as a catalyst, 19.22 per cent. of the possible amount of transformation was effected in 71 hours, that is, calculating as before, 0.30 per cent. per hour, or 0.005 per cent. per minute. Then, if in transforming an ester with four equivalents of the alcohol, we use 0.01 equivalent of sodium alcoholate, the reaction would proceed at the rate of 3 per cent. per minute, approximately, while if we use instead 0.01 equivalent of hydrochloric acid, the velocity would be only about 0.0007 per cent. per minute. Thus the sodium alcoholate is something like 4000 times as efficient as the equivalent amount of hydrochloric acid. It is well known that sodium hydroxide saponifies an ester enormously faster than hydrochloric acid. As sodium ethylate cannot exist in the presence of benzoic acid we cannot study the formation of an ester from the acid by its agency. In the case of an amide, like benzamide, which is far weaker as an acid than benzoic acid, if we add a quantity of sodium to the alcoholic solution of the amide, the sodium would be partitioned between the alcohol and the amide and some sodium alcoholate would remain as such, and esterification of the amide should be brought about. To test this, 4.1785 grams, or 34.55

millimoles, of benzamide was sealed up with 6.4609 grams, or 130.32 millimoles, of anhydrous ethyl alcohol to which 0.0632 grams, or 2.75 millimoles, of sodium had been added. This mixture was heated 11 hours at 100°. On opening the tube there was a strong odor of ammonia and on pouring the contents into water a globule of ester separated out. To neutralize this 18.5 cc. more of tenth-normal acid was required than could be accounted for by the sodium ethylate present. The mixture was distilled with steam and the distillate, which contained globules of ester, heated with standard alkali and titrated back. The saponification of the ester yielded acid to neutralize 10.5 cc. tenth-normal alkali. Thus about 3 per cent. of the amide had been esterified. A mixture of about the same amounts of benzamide and alcohol, but without the sodium, was heated in the same bath for the same time but gave no detectable amount of ammonia or of ester. Meta- and paranitrobenzamides, which as acids are far stronger than benzamide, were tried both in methyl and in ethyl alcohols with sodium alcoholates, but no ester could be detected.

Without Catalyst.—In order to reach the equilibrium in reasonable time, this work was done at about 220°. The glass tubes, after being sealed at one end and drawn down to a narrow neck at the other, were well extracted with hot dilute hydrochloric acid before use. After weighing in the desired amounts of esters and alcohols, the tubes were sealed and heated in the steel tube previously described.[1] Four experiments were made, two starting with methyl, and two starting with ethyl ester. The proportions were purposely made as various as possible, two mixtures containing excess of the ester and two, a large excess of the alcohol. The process of analysis was exactly as described above. The first mixture was heated 40 hours, most of the time at 187°. As will be seen below, this failed by a considerable amount to reach the expected equilibrium, hence the other three were heated for a longer time and at a higher temperature. The second was heated 24 hours at 150°, 20 hours at 180°, and 42 hours at 208° to 215°. The third was heated about 57 hours, the temperature

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[1] THIS JOURNAL, **43**, 489.

varying from 209° to 218°. On opening this tube there was a slight pressure. The fourth was heated about 70 hours at from 200° to 210°. All of the reaction mixtures were slightly yellow in color. The results are given in the usual form in Table IX, except that duplicate determinations of the density are given and the percentage calculated for both of them:

Table IX.

		Methyl ester and ethyl alcohol.		Ethyl ester and methyl alcohol.	
Ester in grams		13.085	13.258	11.874	12.730
Alcohol in grams		5.513	3.727	1.787	4.754
Ester in millimoles		96.17	97.45	79.12	84.82
Alcohol in millimoles		119.71	80.93	55.06	146.47
Density	1	1.06614	1.06800	1.06194	1.07172
	2	.....	1.06805	1.06193	1.07168
Per cent. of methyl ester, found	1	53.76	57.99	43.95	66.40
	2	...	58.10	43.93	66.32
Per cent. of methyl ester, calculated		47.91	57.96	44.34	66.41
Difference		5.85	0.08	0.40	0.04

The first mixture had evidently not reached equilibrium. In the third mixture the per cent. found is rather far from the calculated, but the value found is on the side of the equilibrium from which it was being approached and the error may be due in part to insufficient heating, the time in this case being a little less than in the other two. In the last mixture the water present was 62.3 mg. or 3.35 millimoles. The presence of this water did not influence the partition of the benzoyl between the methoxyl and the ethoxyl. The agreement between the percentages found and those calculated may be regarded as satisfactory.

The Partition of Benzoic Acid between Ethyl Alcohol and Ethyl Mercaptan.

In a former paper[1] the two reactions,

$$(11).\ C_6H_5COOH + HOC_2H_5 \overset{4}{\underset{1}{\rightleftharpoons}} C_6H_5COOC_2H_5 + H_2O,$$

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[1] This Journal, **43**, 502.

$$(12).\ C_6H_5COOH + HSC_2H_5 \xrightleftharpoons[25]{1} C_6H_5COSC_2H_5 + H_2O,$$

were compared and it was concluded that "alcohol is 100 times as efficient in forming esters as its homologue, mercaptan." This figure, 100, was obtained by dividing 4, the value of the constant k in the first reaction, by 0.04, the value of the constant in the second reaction. Since the partition factors used in this paper are the square roots of these constants, the partition ratio between alcohol and mercaptan should have been obtained by dividing $\sqrt{4}$, or 2 by $\sqrt{0.04}$, or 0.2, which gives 10. That is, alcohol is just 10 times as efficient as *mercaptan in forming esters*, or in the contest for benzoyl.

The results cited below are regarded as only preliminary, as it is evident that the mixtures were not sufficiently heated, but even they show clearly that alcohol and mercaptan replace each other according to the formulation

$$(13).\ C_6H_5COOC_2H_5 + HSC_2H_5 \xrightleftharpoons[10]{1} C_6H_5COSC_2H_5 + HOC_2H_5,$$

and that the reaction is reversible.

The ethyl benzoate and mercaptan, in the one case, and the ethyl thiolbenzoate and alcohol in the other case, were weighed into small hard glass tubes and heated for about 45 hours to about 220°. The amounts of ester used were about 0.300 gram and the amounts of the alcohol or mercaptan were equivalent to from 1 to 4 times this amount of ester. On opening the tubes no appreciable pressure was found, but lead acetate solution, through which the vapors from the mixtures were passed, showed traces of hydrogen sulphide. The contents of each tube were emptied into a small test tube which was stood in boiling water while a stream of tiny bubbles of dry hydrogen was made to pass through the mixture for about half an hour. The sulphur in the mixture was determined by a modification of the method of Morse and Gray.[1]

The weight of sulphur found in the combustion of a weighed amount of the resulting ester mixture was multiplied by the

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[1] This Journal, **35**, 451.

proper factor to obtain the weight of thiol ester in the mixture and the difference assumed to be ethyl benzoate. From these weights the equivalents were calculated in the reaction product. Now if a be the equivalent of thiol, —SC_2H_5, whether originally present as $C_6H_5COSC_2H_5$ or as HSC_2H_5, and b be the equivalent of ethoxyl, —OC_2H_5, whether present as $C_6H_5COOC_2H_5$ or as HOC_2H_5, then the partition of the benzoyl should be in the ratio a/bx, in which x is the ratio of the partition factor of alcohol to that of mercaptan, and if c and d are the equivalents of thiol and oxygen esters found by analysis, then $a : bx : : c : d$ and $x = ad/bc$.

In Table X are given the values of a, b, c, d and x for the experiments starting with thiol ester and mercaptan and in Table XI those for experiments starting with oxygen ester and mercaptan:

Table X.

a	1.957	1.726	1.420	1.840	2.432	2.118
b	3.946	5.298	5.483	2.443	3.309	3.828
c	0.1649	0.1047	0.0887	0.2760	0.3760	0.2347
d	1.368	1.327	1.092	1.283	1.766	1.181
x	4.11	4.13	3.19	3.50	3.45	2.25

Table XI.

a	3.928	5.123	3.469	3.785	2.879	4.139
b	2.014	2.285	2.622	1.845	1.974	1.676
c	0.0549	0.0737	0.0875	0.1312	0.1386	0.1249
d	0.5837	1.602	2.312	1.443	1.486	1.296
x	20.7	48.8	35.0	22.6	15.6	25.6

It is apparent that equilibrium had not been reached in any of the experiments, but if in both series something like the same proportionate approach towards equilibrium had been made, the value of x to which both series converge might be obtained by putting $x = \sqrt{3.44 \times 28.0}$, in which 3.44 and 28.0 are the average values of x from Tables X and XI, respectively. This gives $x = 9.8$, which is near the value 10 deduced above from the previous work.

The Partition of Benzoyl between Hydroxyl, Ethoxyl and the Amido Group.

The extension of this reasoning to the equilibrium between ammonium benzoate and benzamide and water is interesting. In the esterification of benzoic acid by alcohol and in the transformation of ammonium benzoate into benzamide and water, as has recently been shown,[1] the limits, and hence the partition factors, are of the same order, the limits being 66.7 and about 75 per cent., respectively, and the factors, 1.991 and 2.

(14). $C_6H_5COOH + HOC_2H_5 \underset{1}{\overset{4}{\rightleftarrows}} C_6H_5COOC_2H_5 + HOH.$

(15). $C_6H_5COOH + NH_3 \underset{1}{\overset{9}{\rightleftarrows}} C_6H_5CONH_2 + H_2O.$

It would appear then that alcohol and ammonia would partition benzoyl between them in the ratio of about 2 : 3, that is, that ammonia should transform about 60 per cent. of an equivalent amount of ethyl benzoate into benzamide.

Efforts to test this by heating benzamide with alcohol led to complicated results which have recently been reported upon,[2] but an experiment starting from the other end was more successful, though perhaps not absolutely satisfactory. Ethyl benzoate to the amount of 7.826 grams, or 52.15 millimoles, was saturated with dry ammonia at —20°, sealed up and heated 14 hours at 200°. On cooling, a small amount of crystals formed. It was reheated for 45 hours more at about 200°, and analyzed by distillation with magnesium hydroxide and then with caustic soda. This gave 15.07 millimoles of benzamide and 0.036 of ammonia. Assuming that equilibrium had been reached and calculating in the usual way, this gives in reaction (16) the forward velocity as 170 times the reverse and the equilibrium constant as 170, then the partition factor is $\sqrt{170}$ or 16. From this it appears that if the ammonia had been present in amount equivalent to the ester,

(16). $C_6H_5COOC_2H_5 + NH_3 \underset{1}{\overset{170}{\rightleftarrows}} C_6H_5CONH_2 + HOC_2H_5.$

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[1] This Journal, **44**, 76.

[2] *Ibid.*, **45**, 38.

equilibrium would have been reached when 92.88 per cent. of transformation into amide and alcohol had taken place. Putting it in another way, in reaction (16) ammonia shows itself 13 times as active as alcohol, in reaction (14) alcohol appears to be 2 times as active as water, then ammonia should be 26 times as active as water, while in reaction (15) it appears to be only 3 times as active as water in the contest for benzoyl. It is not necessary to seek far for an explanation of the discrepancy. In the mixture represented by reaction (15), part, probably the larger part, of the ammonia is in combination with the acid as ammonium benzoate and it is only the free ammonia that is carrying on the reaction. If we assume that 26 is the true partition factor for the $—NH_2$ as compared with the —OH group in reaction (15), then $26/3 = 8.67$. Since the same fraction of the benzoic acid as of the ammonia is taking part in the reaction, $1/\sqrt{8.67}$ or $1/2.94$, equalling 34 per cent., of the ammonium benzoate, is dissociated into benzoic acid and ammonia at the temperature of the experiment, about 210°. This is not an improbable value.

This gives an explanation of the fact observed by Menschutkin[1] that the limit of amide formation shifts toward the amide end with rise of temperature. Measuring the equilibrium between amides and esters at different temperatures may furnish a clue to the dissociation of the corresponding ammonium salts at different temperatures.

The Partition of an Alcohol between Two Acids.

This has been studied in two cases, and though the results are not much more than preliminary, yet they indicate that, in this case also, transformation proceeds, and partition results on the basis set forth in the introduction.

Acetic and benzoic acids are known to give the same esterification limits with ethyl alcohol. Since, for most of the acids quoted in Table II, with the exception of the chloracetic acids which are exceptional in other ways, the limits are practically identical, the limit, and hence the partition factor, for *p*-brombenzoic acid has for the present been assumed

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[1] J. prakt. Chem., [2] **29**, 422.

to be the same as for benzoic acid. According to this, if we heat 25 equivalents of *p*-brombenzoic acid with 100 equivalents of ethyl benzoate, we would expect the resulting ester mixture to contain 25 molecular per cent. of the *p*-brombenzoic ester.

Benzoic Acid and Acetic Acid.—A mixture containing 11.0231 grams of benzoic acid and 13.4856 grams of benzyl acetate, that is, 90.32 millimoles of the acid to 89.85 of the ester, was sealed up and heated 40 hours to about 210°. On opening no pressure was found. The product was shaken out with 60 cc. of water containing 14 grams of sodium carbonate and further treated as were the ethyl and methyl benzoate mixtures above described. Two density determinations in 2.3- and 5.5-gram pycnometers gave 1.09063 and 1.09069, respectively.

To 1.3757 grams, or 6.487 millimoles, of the benzyl benzoate obtained as described below was added 0.9592 gram, or 6.39 millimoles, of benzyl acetate, giving a mixture containing 50.37 molecular per cent. of benzyl benzoate. This had a density of 1.08767. Since in the neighborhood of 50 per cent. the curve representing the relation of density to composition of such mixtures has about the same slope as the straight line joining its extremes (for a verification of this see Figs. I and II), which has a slope of 0.00067 change in density for 1 molecular per cent., this same value may be used in calculating the composition of a mixture having the density above found for the reaction product of the above experiment. Thus it is found that this contained 54.88 per cent. of benzyl benzoate when, according to the assumption made, it should have contained only 50.14 per cent. The error is not surprising when the great differences in properties of the two esters involved are taken into account. The difference in boiling points of the two esters is 111°, rendering a partial fractionation of the mixture during the hydrogen treatment possible. The long treatment of the mixture with sodium carbonate to eliminate the acids is also likely to change its composition somewhat. The experiment indicates, however, that acetic acid is replaced by benzoic acid on approximately equal terms, or, in other words, that benzyl alcohol is partitioned between acetic acid and benzoic acids in approximately the ratio of 1 : 1.

Benzoic Acid and p-*Brombenzoic Acid.*—In order to determine the relation between density and composition of mixtures of the ethyl esters of these two acids, several such mixtures were made up and their densities determined. The results are given in Table XII and graphically in Fig. II.

Table XII.

Ethyl *p*-brombenzoate in grams	0.9282	1.6061	1.9733	2.4688
Ethyl benzoate in g'ms	1.4843	1.0290	1.2241	0.7142
Ethyl *p*-brombenzoate in millimoles	4.053	7.013	8.616	10.779
Ethyl benzoate in millimoles	9.890	6.856	8.156	4.759
Per cent. of brom ester	38.48	60.95	61.72	77.57
Molecular per cent.	29.07	50.56	51.37	67.80
Density of mixture	1.1671	1.2524	1.2557	1.3245

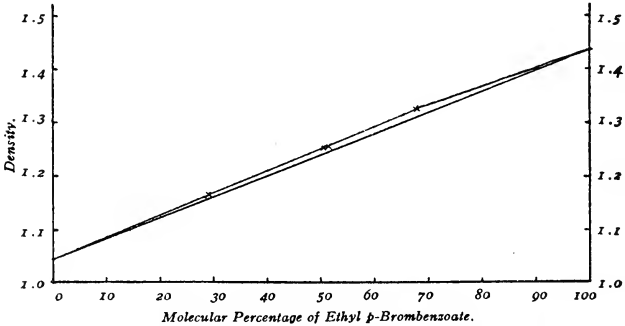

Figure II.—Density of Mixtures of Ethyl Benzoate and *p*-Brombenzoate.

Five experiments were made without any catalyst since the sodium alcoholates are out of the question and, since, in the experiments described above, the hydrochloric acid acted so much on the alcohols to form alkyl chlorides. In the first two experiments benzoic acid and ethyl *p*-brombenzoate were used, and in the other three *p*-brombenzoic acid and ethyl benzoate. Small samples and small pycnometers, holding 1.3 and 1.6 cc., were employed. The first two mixtures were heated about 40 hours to about 210° and the others 43 hours to about the same temperature. On account of the high melting point of the *p*-brombenzoic acid and its comparatively slight solubility in the ester, except at high temperatures, the acid and ester were mixed by tilting the steel tube, in which the small glass tubes containing the mixtures were heated, after it had reached nearly 200°, several hundred times, so that the liquid would run from one end to the other. On opening, in none of the tubes was more than trifling pressure found. The contents of a tube were washed, with the aid of moderate amounts of ether, into a small separatory funnel and shaken with the calculated amount of a saturated sodium bicarbonate solution for ten minutes. The extraction was repeated with 10 cc. portions of the bicarbonate solution, shaking ten minutes each time, till the aqueous extract failed to give any cloudiness on acidification. The extraction of the acids was complete in three or four operations. The ethereal portion was filtered, concentrated, and the ether and water eliminated by passing a fine stream of dry hydrogen for an hour through the mixture in a test tube surrounded by boiling water. The results are given in the usual form in Table XIII. The percentages were taken graphically from the original drawing for Fig. II.

Table XIII.

	p-Brombenzoic ester and benzoic acid.		Benzoic ester and *p*-brombenzoic acid.		
Ester in grams	4.0118	2.9111	3.1590	2.9591	2.9041
Acid in grams	1.5094	1.7275	1.8272	1.7152	0.6795
Ester in millimoles	17.52	12.71	21.05	19.72	19.35
Acid in millimoles	12.37	14.15	9.090	8.53	3.38
Density	1.2998	1.2706	1.1590	1.1629	1.1044
Brom ester per cent., found	62.0	55.0	27.8	26.1	14.0
Brom ester per cent., calculated	58.6	47.3	30.2	30.2	14.9
Difference	1.1	3.5	4.8	3.9	2.8

The agreement is only approximate, though in all cases the value found is on the side from which the equilibrium was being approached, which suggests that a part, at least, of the error may be due to insufficient heating. However, the results show plainly that when either of these acids is heated with the ester of the other, there is a partial replacement, the alcohol being partitioned between the two acids approximately in proportion to the concentrations of the two acids.

Double Decomposition between Two Esters.

A mixture was made of 13 cc. each of ethyl benzoate and benzoyl acetate, sealed up and heated about 44 hours to 210°–216°. The resulting mixture was reddish-yellow with some fluorescence. On opening the tube at room temperature some combustible gas escaped. On distilling the mixture, about 0.3 cc. went over below 110°. This had a density less than 1 and the characteristic odor of ethyl acetate. The bulk of the mixture boiled around 209° to 212° and then the thermometer went up rapidly to about 320° (uncorrected). The portion boiling above 240° had a density of 1.0970 and consisted largely of benzyl benzoate. Two other experiments were tried in which the ester mixture was boiled many hours under a return condenser. The products on distillation behaved in the same way as the above. The higher boiling fractions obtained from these reaction products were united and redistilled. The fraction boiling between 300° and 318° (uncorrected) had a density of 1.1116 (25°/25°), while benzyl benzoate is said to have a density of 1.1114 at 16°.

These experiments show that we have double decomposition between two esters.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
March, 1911.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

PART IV.—THE MEMBRANES.

By H. N. Morse, W. W. Holland and C. N. Myers.

A proper investigation of the membranes which are deposited in the interior of cells is impossible, owing to their inaccessibility. The conduct of the material of the membranes towards reagents of various kinds can be studied outside of the cell, but such study yields little of interest or value, so long as the substances whose pressures are under investigation are known to have no chemical action on the membranes. If we overlook, for the present, the destructive attacks upon the membrane by one or more organisms, the whole question of successful or unsuccessful membranes may be truthfully said to turn upon a considerable number of very obscure physical conditions. If a membrane fails, the causes of failure can, in the first instance, only be guessed at, and, ordinarily, they are finally discovered by a wearisome process of exclusion. Some things pertaining to the membranes can be established *a priori*, and others may be learned by microscopic examination of broken cells. But facts which may be brought to light in such ways relate almost solely to the location of the membranes and their attachment to the cell walls.

The first membranes which were formed by the electrolytic process were deposited *within* the cell wall. But it was clear that with a membrane so located it would be impossible to measure osmotic pressure. The obvious objections to such a position are:

1. Every part of a cell wall is filled at all times with some liquid—either water or a solution; hence, if the membrane is *within* the wall, any solution which is placed in the cell for the purpose of measuring its pressure will be diluted or contam-

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon this subject will be found in This Journal, **26,** 80; **28,** 1; **29,** 173; **32,** 93; **34,** 1; **36,** 1 and 39; **37,** 324, 425, and 558; **38,** 175; **39,** 667; **40,** 1, 194, 266 and 325; **41,** 1, 92, and 257; **45,** 91, 237 and 383.

inated by the liquid filling the wall space between itself and the membrane.

2. Even if the space in question, i. e., that between the interior surface of the cell and the membrane *within*, were filled with the solution whose pressure is to be measured, the portion of it which is nearest the membrane would become and *remain* more dilute than the great body of the solution, owing to the slowness of diffusion in the cell wall.

3. It is only in quite porous cells, or rather in cells with quite large pores, that the membrane *is* deposited within the wall, and a membrane so located, being imperfectly supported, always breaks under moderate pressures.

It was the necessity of moving the membrane from the *interior* of the wall, where it was deposited in the cells of the potters, to the *inner surface*, which led to the elaborate experiments in cell making which were described in part in the first of this series of papers. It was there stated that, when the pores are large, the ferrocyanogen ions penetrate far into the cell wall before meeting those of copper, though never quite to the center of it; and that, as the texture becomes finer—in the sense of diminishing diameter of the pores—they penetrate less far, and the membrane is deposited nearer and nearer to the inner surface of the cell wall. When a certain degree of fineness of texture is reached, the membrane is deposited *upon* the surface, and no danger is to be apprehended that the membranes will not be sufficiently supported from the rear.

The texture of a cell, however, may be *too* fine. A microscopic examination of the best of our cells in which membranes have been deposited shows, not only that they *cover* the walls, but that they also *penetrate* to some extent the pores which open on the inner surface—that the membranes are, so to speak, *rooted* into the walls. To this *penetration* of the wall by the membrane we are inclined to ascribe great importance, for it is to this alone, we believe, that the firm adhesion of the membranes to the surface is due. Moreover, it is probably to the absence of such penetration of the pores by the membrane that the very general failure of membranes made by the diffusion method is to be ascribed.

When a certain degree of fineness of texture is exceeded, the membranes do not adhere well, and it is found, on breaking the cells in such cases, that the penetration of the wall by the membrane is very slight.

There are a number of observations connected with the location of the membrane on the inner surface of the cell and its attachmennt to the wall behind which are worthy of notice in this place. The first of these relates to the distribution of the solvent after it has passed through the membrane into the enclosed solution. It has been maintained that the osmotic pressure cannot be correctly measured without an *active stirring* of the solution; that, otherwise, the entering solvent is not distributed with sufficient rapidity. We confess that we, also, were apprehensive for a long time that it would be necessary, after perfecting the cell, to complicate the work of measuring and to increase its difficulty by the introduction of stirring devices. But, to the best of our judgment at the present time, our fears were without foundation. With the entering water discharging from the free surface of the membrane directly into the solution, currents, caused by differences in density, should be established which would tend to sweep the diluted portions of the solution constantly away from the membrane towards the interior; and we have never observed anything in the conduct of the cells which indicated that these did not suffice to bring about quickly a uniform distribution of the solvent which enters from without. The symptom which would be watched for in this connection would be extreme slowness on the part of the solutions in developing their maximum pressures. But we have had a concentrated solution attain its maximum pressure in less than 24 hours, and maintain it thereafter for several weeks, except for such slight fluctuations as could reasonably be ascribed to *thermometer* and *barometer* effects. The only condition with which we have been able to connect the time consumed in developing the highest pressures is the *thickness* of the membranes.

It has been observed that when—owing to some accident to the regulating devices—there is a considerable and rapid fall in the temperature of the solutions in the cells, it is rarely possible thereafter to secure a successful measurement of pressure. When the temperature of the bath is restored, it is found, as a rule, that the membranes give evidence of having been ruptured during the fall in temperature. It is supposed in such cases—though the explanation cannot be verified—that the membranes have been *detached* from the walls in places.

Whenever a membrane, through long use and frequent mending, has become too thick for prompt action, it is very desirable to replace it by a new and more active one. The operation would seem to be a very simple one, but we have rarely succeeded in performing it successfully. At first, the old membranes were removed with dilute mineral acids; but, having failed to obtain good new membranes in their places, dilute ammonia, ammonium tartrate, and electrolysis in the presence of dilute tartaric acid were resorted to in turn, with indifferent success, however, so far as the character of the new membranes was concerned. The reason for this conduct on the part of cells whose membranes have been removed is obscure. The only tentative explanation which commends itself is that the surfaces of the cell walls, or the mouths of the pores which open upon them, have in some way been modified by the reagents, so that the new membranes do not secure as firm a foothold as they do in new cells. A remedy which has suggested itself is to grind the surface from which the membrane has been removed, but this is always an uncertain operation, because no part of the surface to be removed by grinding can be seen. Another remedy which has been tried with partial success is the rebaking of the cells at high temperatures. This is a practice which was frequently resorted to with the potters' cells, and sometimes with our own, for the purpose of diminishing the size of the pores by shrinkage. In the case of the potters' cells, it was not successful because of the unevenness of the texture. After they had been reburned at the highest practicable temperatures, some of the pores were still too large to permit the building up of strong membranes. The improvement in this way of cells from which membranes have been removed is limited by the fact that at very high temperatures the glaze volatilizes, and may plug the pores, making it necessary to grind away both the interior and exterior surfaces of the cell.

The process of depositing the membranes has been described in earlier papers, but it will be necessary to restate its main features in order to secure a basis for such comments as we think should be made.

The first step to be taken with the finished cell is to expel the air from the pores and to replace it by water. This has been accomplished from the first by means of "electrical endosmose," that is, by electrolyzing a dilute solution of some salt which nearly fills the cell and in which it is immersed to the lower edge of the glazed portion. The inner electrode serves as cathode, and provision is made for the automatic removal of the water which is drawn through the porous wall into the cell. At intervals the electrolysis is stopped, for the purpose of mixing the liquid which has been removed by the siphon with the liquid in the outer vessel. When it is judged that all the air has been removed from the porous wall, the cell is taken out, emptied and rinsed with pure water. It is then soaked for a time in distilled water, which is frequently renewed. Lastly, it is filled with, and partially immersed in, pure water, and the electrolysis is repeated. When the conductivity, after frequent renewals of the water, has fallen nearly to that which is normal for the distilled water itself, the cell is ready for the deposition of the membrane. If the membrane is not to be deposited immediately, the cell is placed and kept until needed in water in which a little thymol or formaldehyde has been dissolved. The reason for this precaution will appear later when the subject of the *infection* of the membrane is taken up. It is also well to *boil* all the water which comes in contact with the cell, both that which is used in making the solution for the "endosmose," and that which is employed in renewals and in rinsing the cell. Moreover, any further precautions against infection which the prevailing conditions may suggest are by no means superfluous.

The dilute solution which was first employed to sweep the air out of the pores of the cell wall was a 0.005 normal one of potassium sulphate; but, since the slower cations are supposed to carry about with them larger "atmospheres" of water, it was thought that lithium sulphate should give a much larger "endosmose" than the potassium salt. And this was found to be the case. On extending the comparison to several salts with a common anion, the following rule was found to hold good for the substances investigated:[1] "*The quantities of water carried through the porous wall of a cell, under identical conditions, are inversely proportional to the relative velocities of the various cations divided by their respective valencies.*" Since that time, only solutions of lithium sulphate have been used to expel the air from the cell walls.

The arrangement for the deposition of the membrane is as follows: The anode—a copper cylinder—is placed in an empty glass vessel, and within the cylinder is set the cell, which is closed by a rubber stopper carrying the cathode (a platinum cylinder), a funnel with a stem nearly long enough to reach the bottom of the cell and an overflow tube. The circuit is closed, and, as nearly simultaneously as possible, the cell and the vessel outside of it are filled, each with its appropriate solution. The solutions, potassium ferrocyanide and copper sulphate, are of tenth-normal concentration. The voltage which is employed is 110. At first, the resistance is very high, owing to the fact that the cell wall is filled with nearly pure water. Very soon, however, the current begins to increase, and within a short time it attains a maximum. It then drops again steadily for two or three hours and perhaps longer, when a maximum of resistance is reached. If the electrolysis is continued very long after the current has once become constant, the resistance begins to fall again. As soon as the period of decreasing resistance is reached, the cell is removed, rinsed with water, and immersed in a bottle containing a dilute solution of thymol. Here it is allowed to soak from one to three days, with an occasional renewal of

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[1] THIS JOURNAL, **36**, 28.

the thymol water, when it is again treated as in the first instance, etc. The resistance rises higher and higher on successive treatments, until a permanent maximum is reached, when the membrane is regarded as ready for its first trial.

The membrane is readily attacked by dilute alkali, hence, during the deposition, the cell is flushed out every two minutes with a fresh solution of potassium ferrocyanide.

The final resistance of the membrane depends both upon the cell and the temperature at which it is deposited. The closer the texture of the cell wall is, the higher will be the resistance at a given temperature, and the lower the temperature is, the higher will be the resistance of the membrane in a given cell.

The cell is placed in a bath of constant temperature for the deposition of the membrane, and usually in one having the temperature at which the cell is afterwards to measure pressure. It has been found that it may be deposited advantageously either *at* or *above*, but not *below*, the temperature at which the cell is to be used. An analogous observation is the fact that, when a cell has been used at one temperature, it is much easier to prepare it to measure at a lower temperature than at a higher one. It is for this reason that we prefer, whenever it is practicable, to measure pressures first at the highest temperature and then at each of the lower temperatures in regular succession.

The copper ferrocyanide membrane has never been known to give a maximum pressure on the first trial. Some of the other membranes which we have under observation, e. g., the ferrocyanide of nickel, seem likely to prove superior to it in this respect. The cell is set up for the first time with a concentrated solution—usually a weight-normal one—and under very little mechanical pressure. That is, the meniscus, when the cell is closed, is left in the lower part of the manometer. The purpose of having it start from this position is to learn as much as possible about the membrane from the conduct of the meniscus while the mercury is being pushed up the tube by the increasing osmotic pressure. If the meniscus rises continuously, without change of form, until the maximum pressure is nearly reached, there is reason to believe that a comparatively few repetitions of the membrane-forming process will be required to bring the cell into perfect condition for the measurement of pressure. If, on the other hand, the meniscus rises irregularly, stopping from time to time and changing its form, it can be predicted that two or three, and perhaps four, months will be required to put the membrane in good condition. On the first trial, the solution within the cell is made 0.1 normal with respect to potassium ferrocyanide, and the water in which the cell is placed contains a supposed osmotically equivalent quantity of copper sulphate. The occasional stopping of the meniscus on its way up the tube and the change in its form are believed to be due to a breaking of the membrane, and the resumption of its course is supposed to indicate that the rent has been mended, or at least that the mending process has proceeded so far that the osmotic pressure is increasing more rapidly than the membrane is leaking.

Whatever may have been the conduct of the membrane during the first trial, the cell, after it has been opened and emptied, is thoroughly rinsed with water containing thymol. It is then allowed to soak for two or three days in a closed bottle filled with a dilute solution of thymol, which is frequently renewed. At the close of this period it is resubjected to the membrane-forming process, and later it is set up for a second trial. The quantities of the membrane-formers which are used on the second and subsequent trials depend on the conduct of the membrane during the previous trial. They are reduced as fast as may be until the liquids within and without the cell are 0.01 osmotically normal with respect to the two salts, due allowance being made for their known electrolytic dissociation.

The procedure described above is continued until a perfect membrane is obtained, that is, until the cell is able to maintain for an indefinite period the known *maximum* osmotic pressure of a normal solution of cane sugar. That the cell maintains a *constant* pressure for a long period is not a sufficient test of the membrane; for it often happens that the pressure remains perfectly constant for a long time—indefinitely, so far as we know—when the pressure observed is not the *maximum* pressure of the solution which was put into the cell. When this occurs, the solution, on opening the cell, is found to have suffered some dilution. The probable explanation is that, at some period, the membrane has broken and permitted some of the solution to escape, and that the rent has afterwards been effectually mended by the membrane formers, so that the observed *constant* pressure is really that of a *diluted* solution—diminished, of course, by the adverse pressure of whatever has escaped from the cell. Right here is one of the most fruitful opportunities for self-deception in the measurement of osmotic pressure, and it cannot be too strongly emphasized that mere *constancy* of pressure is of little value, except when it is proved conclusively at the close of the experiment that the solution has suffered no dilution while in the cell.

The time required to perfect a new membrane varies greatly with different cells. The shortest time in which it can be done is about one month. If, unfortunately, the cell once becomes "infected," three or even four months may be necessary. In some cells it has been found quite impossible to build up a good membrane; but, in such cases, on breaking the cells, defects—usually cracks, the existence of which was previously unsuspected—have been revealed.

A cell which is to be used for the measurement of pressure at a given temperature is maintained at all times at that particular temperature until the work is finished. To this end, no liquids having any other temperature are allowed to come in contact with it, and it is never kept longer than is necessary out of its constant temperature bath.

All solutions of which the osmotic pressures are to be measured are made 0.01 *osmotically* normal with respect to potassium ferrocyanide, the salt being supposed to be completely dissociated at that dilution. The exact quantity of the salt which is dissolved in each 100 grams of water is 83.9 milligrams. The solutions are also made 0.001 normal with respect to thymol, the purpose being to prevent the growth of *penicillium* in case the solutions or the membranes have become infected.

To each 100 grams of the water in which the cells are placed during a measurement, there are added 123.9 milligrams of crystallized copper sulphate, which quantity is required—if the salt is completely dissociated—to give a 0.01 osmotically weight-normal solution. There is also added enough thymol to make a 0.001 normal solution of that substance. The solutions and the water in which the cells are placed are therefore equally concentrated so far as the thymol is concerned, and they are supposed to contain osmotically equivalent quantities of the membrane-forming salts. Several attempts have been made to ascertain, by means of open manometers, whether the quantities of the two salts which are used are in reality osmotically equivalent; but, owing to complications which will be explained later, it was impossible to arrive at any satisfactory conclusion. The difference between the osmotic pressures of the two, if any exists, is very small.

After finishing an experiment, the cell is emptied, thoroughly washed, and then allowed to soak from two to three days in a dilute solution—usually 0.001 weight-normal—of thymol, which is renewed at least twice a day. It is then ready to be prepared for another measurement of pressure. The preparation consists in subjecting the cell to one or more repetitions of the membrane-forming process, until the high resistance of the membrane indicates that its condition is again satisfactory. An interval of one or two days is usually allowed between any two repetitions of the process for the purpose of soaking the cell in thymol water.

The solution which was removed from the cell at the conclusion of the experiment is compared in the saccharimeter with a reserved portion of the original solution, and if any loss in rotation is detected, the experiment is rejected as unsatisfactory on the ground that the *perfect maintenance of concentration* in the cell contents is the only safe criterion in the measurement of osmotic pressure.

The conduct of a new membrane is very different from that of an old one, especially in respect to the time required by the solutions to reach the maximum pressures. When the membranes are quite new, the highest pressures are usually reached in less than 24 hours; but as a membrane grows thicker (and probably more dense) in consequence of the frequent and many repetitions of the process of deposition and mending, the cell becomes slower and slower until, after from 12 to 24 months, a solution may consume a whole week in developing its maximum pressure. When this stage in the history of a membrane is reached, the cell is discarded, though it is usually still perfectly fit for the measurement of pressure if given enough time. The principal reason for discarding the "old-timers" is that the labor of preparing a sufficient supply of manometers is too great to permit cells to remain for long periods in the baths.

The following records of two determinations of osmotic pressure will illustrate the difference, as regards the time required for the development of maximum pressure between an excellent new membrane and an old one which, though exexceedingly slow, is otherwise in excellent condition for the correct measurement of pressure.

I. New Membrane.

Weight-normal concentration of solution, 0.9. Temperature, 25°. Time of setting up the cell, Jan. 20, 1910, 4.00 P.M.

Date.	Osmotic pressure. Atmospheres.	Date.	Osmotic pressure. Atmospheres.
Jan. 20, 10.00 P.M.	24.127	Jan. 23, 10.00 A.M.	24.102
Jan. 21, 1.00 P.M.	24.148	Jan. 24, 10.00 A.M.	24.125
Jan. 22, 9.00 A.M.	24.120		
		Mean pressure,	24.126

II. Old Membrane.

Weight-normal concentration of solution, 0.6. Temperature, 25°. Time of setting up the cell, Nov. 10, 1910. 4.00 P.M.

Date.	Osmotic pressure. Atmospheres.	Date.	Osmotic pressure. Atmospheres.
Nov. 16, 5.00 P.M.	15.654	Nov. 20, 10.00 A.M.	15.628
Nov. 19, 8.00 P.M.	15.612	Nov. 21, 9.00 A.M.	15.629
		Mean pressure,	15.627

In the case of the new membrane cited above, the maximum pressure was reached in 6 hours; while in that of the old one, 6 full days were required. In one instance on our records, when a very old membrane was used in the experiment, the pressure reached a maximum on the *10th day* and remained constant for 12 days thereafter, when the cell was opened. The measurement was an excellent one, and the only defect of the cell was the excessive slowness with which the water passed through the membrane into the solution.

We have never been able to discover that the concentration of the solution has any influence on the time consumed in developing the final pressure, but it is impossible to make any satisfactory quantitative comparisons for the purpose of answering this question, since no two membranes conduct themselves exactly alike, nor does a given membrane ever conduct itself in precisely the same manner in two consecutive experiments. We are under the impression, however, that the rate at which water will make its way into a solution in any given case is dependent principally on the thickness of the membrane and on the difference between the final and the prevailing pressures. We are also under the impression that the membranes are more active at the higher than at the lower temperatures. But here again, it is impossible to secure any satisfactory quantitative evidence.

The fact that time—and in the case of old cells, a great deal of it— is required for the passage of water through the membranes leads to two very troublesome phenomena in the measurement of osmotic pressure, i. e., to what we have designated, for want of more appropriate names, as *thermometer effects* and *barometer effects*. The first are due primarily to fluctuations in the temperature of the bath, which are followed, of course, by changes in the volume of the solutions. Suppose, after the maximum pressure has been developed in a cell, the temperature of the solution is raised a little above the normal, an increase of pressure results, which should be followed by an immediate discharge of water outward and a slight concentration of the solution. If the discharge were instantaneous, no particular harm would be done; for the final increase in concentration would be very slight, and the osmotic pressure for the higher temperatures, which is known, would be correctly determined. But the discharge of the necesssary quantity of water is by no means instantaneous. It lasts for hours, and in the case of old membranes, it would continue possibly for days before coming to an end. In the meantime, the gas in the manometer is under the osmotic pressure of the solution plus a mechanical pressure due to the expansion of the solution. If, on the other hand, the temperature falls below the normal, a contraction in the volume of the solution follows, and the gas is under less than the full osmotic pressure until the requisite amount of water has made its way inward through the membrane.

The only remedy for *thermometer effects* is an exact regulation of temperature. But we have never been able to eliminate them entirely, though the fluctuations in the temperatures of the baths rarely exceed 0°.02. The mischief which a falling temperature may make with the correction for meniscus is too obvious to require explanation.

Barometer effects are of an analogous nature. The fluctuations in barometric pressure, according as they are upwards and downwards, are followed by the passage of water inward or outward through the membrane and the correction for atmospheric pressure is, at any given time, very uncertain unless the transference of the solvent is finished. It is for this reason that we have come to dread seasons of highly variable atmospheric pressure.

The highest barometer which has been observed in the course of this work was 785 mm., while the lowest was 735 mm. The difference, 50 mm., amounts to 6.58 per cent. of an atmosphere, which is a relatively large proportion of the osmotic pressure of the more dilute solutions. An error so large as this could not be committed in correcting for atmospheric pressure, but the possible mistakes are considerable during seasons of large and rapid change in the height of the barometer—especially when the membranes in use are old and "slow." The only remedy for *barometer effects* is, of course, the maintenance of constant atmospheric pressure over the water in which the cell is placed during a measurement, but this is impracticable at present. Some scheme for this purpose will have to be devised, however, when the measurement of the osmotic pressure of very dilute solutions is undertaken.

The evil consequences of the slow passage of the solvent through the membranes, whether *thermometer* or *barometer effects*, are minimized as far as possible in the following ways: (1) Only cells which contain the newest, and consequently the most active, membranes are employed in the measurement of the pressure of the most dilute solutions; (2) the experiments with dilute solutions are undertaken only when the barometer seems likely to remain fairly constant for a considerable period; (3) when the height of the barometer is fluctuating to an unusual extent, the cells are allowed to remain a longer time in the baths; (4) cells in which the membranes have become very slow through long use and repeated mending are discarded, notwithstanding the fact that most of them, except for the *thermometer* and the *barometer effects*, are still efficient.

Thermometer and *barometer effects* can be detected in every record of the measurement of osmotic pressure which we shall present in the later papers. Except for these, the pressure in a cell with a membrane which does not leak, after it has once reached a maximum, should remain perfectly constant as long as the cell is left in the bath. That none of our membranes have leaked is proved by the fact that none of the solutions suffered any loss in rotation. And yet it will be observed, on inspecting the records, that there were, in every instance, slight fluctuations in pressure. They are undoubtedly to be ascribed to the fact that the solvent cannot get through the membranes fast enough to compensate quickly the slight changes in the temperature of the baths and the considerable variations in the pressure of the atmosphere.

It will now be seen why we failed with open manometers to discover with certainty whether our two membrane-formers, in the quantities used, are in reality osmotically equivalent. The difference, if there is any, is smaller than the possible errors due to *thermometer* and *barometer effects*. To investigate minute differences in osmotic pressure, it will be necessary to have both a perfectly constant bath and a perfectly constant atmospheric pressure.

There is one other point which may be mentioned by way of anticipation in connection with the rate of passage of the solvent through membranes. We have some reason for believing that when the osmotic pressure of electrolytes is studied, it will be necessary to employ *very thick* membranes, and probably membranes of *very small area*. If so, the *thermometer* and *barometer effects* will then be much more formidable than they have been hitherto.

The question as to how long the cells should be kept in the bath, after having once developed what appears to be the maximum pressure, is an important one. We have observed that when a cell once reaches its highest pressure and holds it for 20 hours—with only such fluctuations as can reasonably be ascribed to *thermometer* and *barometer effects*—it may be relied on thereafter to maintain that pressure as long as the cell is left in the bath; or, more definitely, for at least six weeks, since that is the longest time we have had a cell under observation.

In two instances, among the approximately 150 determinations which will be reported, the cells remained in the bath 12 and 13 hours, respectively, after having developed maximum pressure, when they were removed because of accidents to the electrical appliances. In six other instances, the times were 19, 20, 21, 21, 23, and 23 hours. Fifteen remained in the bath 24 hours after reaching the highest pressure, and twenty-five between 25 and 30 hours. Fourteen remained between 30 and 40 hours, and thirty-two between 40 and 50 hours. All the others—about one-third—remained more than 50 hours, and among them three for 4 days, four for 5 days, one for 9 days, one for 11 days and one for 13 days.

It has been the policy to keep the cells in the bath until we were certain from previous experience that no further change in osmotic pressure was to be expected, and *as much longer* as the current supply of manometers and bath space would permit.

There are appended the daily records of two cells, one of which remained in the bath 13 days and the other 11 days after reaching maximum pressure. Neither solution suffered any loss in rotation. The first is a good example of a comparatively young membrane which is very active, as is proved by the fact that the maximum pressure was reached in less than 24 hours. The second is an equally good example of an old and slow (though by no means decrepit) membrane, as is shown by the fact that it required *8 days* for the development of the maximum pressure. In both cases, the apparent fluctuations in osmotic pressure are confined to the second decimal place, and they are smaller from day to day than were the corresponding fluctuations of the barometer. The *lower* osmotic pressures correspond in general to the *higher* barometric pressures, and *vice versa*. This is characteristic of *barometric effects*. That is, owing to the lag of the water in passing through the membrane, the correction for atmospheric pressure is *too large* when the barometer is *high*, and *too small* when the barometer is *low*.

Table I.

Weight-normal concentration of solution, 0.8. Temperature, 25°. Time of setting up cell, Jan. 4, 1910, 3.00 P.M. Time of first reading, Jan. 5, 1910, 9.00 A.M.

Time.	Pressure. Atms.	Time.	Pressure. Atms.
Jan. 5	21.281	Jan. 12	21.238
Jan. 6	21.253	Jan. 13	21.266
Jan. 7	21.256	Jan. 14	21.257
Jan. 8	21.281	Jan. 15	21.249
Jan. 9	21.280	Jan. 16	21.249
Jan. 10	21.258	Jan. 17	21.246
Jan. 11	21.238	Jan. 18	21.264
		Mean pressure,	21.258

Table II.

Weight-normal concentration of solution, 0.2. Temperature, 20°. Time of setting up cell, Dec. 15, 1910, 12.00 M. Time of first reading, Dec. 23, 1910, 9.00 A.M.

Time.	Pressure. Atms.	Time.	Pressure. Atms.
Dec. 23	5.080	Dec. 29	5.062
Dec. 24	5.086	Dec. 30	5.058
Dec. 25	5.071	Dec. 31	5.035
Dec. 26	5.060	Jan. 1 (1911)	5.033
Dec. 27	5.061	Jan. 2	5.035
Dec. 28	5.077	Jan. 3	5.042
		Mean temperature,	5.058

We come now to a calamity which for four years has delayed, and which continues to delay, the progress of the work more than all other difficulties combined, that is, to the *infection* of the membrane by the fungus *penicillium glaucum.* We are not certain that this is the only species of infection against which we have to contend, but it is certain that the membranes which are attacked by the *penicillium* are quickly ruined, and that they can only be restored by months of painstaking labor. Our first introduction to the pest was described[1] as follows: "*Soon after beginning the measurement of the osmotic pressure of glucose solutions, there appeared upon one of our cells an abundant growth of a fungus which, upon examination, was found to be* penicillium. *Within a few days, it appeared upon one after another of the remainnig cells until all were affected in the same manner as the first. We then exposed several solutions of glucose to the air of the laboratory, and the fungus appeared in all of them in a short time. We had had no similar experience previously, though we had worked with solutions containing invert sugar for more than two years, and the conditions under which we were working were, in general, unfavorable to the fungus. The sudden prevalence of* penicillium *spores in the atmosphere of the laboratory could, however, be accounted for, though it had not been anticipated. At the time, certain changes were in progress in the lower part of the building, which involved the tearing away of old walls, and the*

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[1] This Journal, **36**, 34.

atmosphere of all parts of the laboratory was, in consequenec, in a somewhat dusty condition."

We have been unable to exterminate the *penicillium*, and we are unable to say precisely how it destroys the membranes, but it is suggested that possibly it finds in the ferrocyanide of copper a supply of nitrogen which it is able to assimilate. It is characteristic of a membrane which has been attacked by the fungus that it can withstand little or no pressure, and always leaks when the cell is set up for the measurement of pressure.

The same paper contains an account of the search which was made for a poison which would kill the fungus without injury to the membranes. Of those tested, two, hydrocyanic acid in gaseous form and thymol, were found to destroy it and to do the membranes no harm. The latter was selected because it is the more easily handled and is the safer of the two.

Since then, every liquid which comes in contact with the cells has been made 0.001 weight-normal with thymol, whether it is the solution whose pressure is to be measured, the water in which a cell is placed during a measurement, or the water in which it is soaked when not in use. The thymol water in which the cells are immersed at all times when they are not otherwise employed is kept in salt bottles which can be tightly closed or in glass jars with closely-fitting covers. More recently, the dry parts of the baths are frequently washed with formaldehyde, and phenol is added to the water in them. Open vessels containing formaldehyde are kept in the constant temperature air spaces above the water baths, and the vapors of it are distributed by means of fans. The rooms in which the baths are located are likewise disinfected from time to time with formaldehyde. Nevertheless, the membranes occasionally become infected. The first evidence of infection is usually the fact that membranes, which were previously rendering satisfactory service, are leaking, and fail to recover readily their fully semipermeable character when resubjected to the membrane-forming process.

The present process of renovation is as follows: The cell with a membrane which has been injured by *penicillium* (or other organisms) is placed in a *saturated* solution of thymol and allowed to remain for several days. It is then soaked out in the usual—more dilute—thymol solution and subjected to the membrane-forming process. If the membrane shows decided improvement after the first course of treatment, it is repeated again and again until the cell is able to develop the highest pressure and to maintain it for a long period. If the membrane does not respond readily to the treatment just described—that is, if it does not show marked improvement—it is placed under a bell jar with a vessel containing potassium cyanide, and hydrocyanic acid is liberated by introducing dilute acid through a funnel tube having a stopcock. After an exposure of from one to two hours, the cell is removed and soaked out in thymol water, after which it is treated as described above. We have also tried soaking infected cells in dilute solutions of formaldehyde, but we are not yet convinced that such treatment is harmless to the membranes.

The following statement will serve to give an idea of the time and trouble necessary for the renovation of an infected membrane. When the cells which had been in use during the winter and spring of 1909 were put away in June for the summer, all the membranes were in perfect condition. On resuming work the first day of October, it was found that most of the cells were infected. The process of restoration was begun at once and was prosecuted thenceforward without interruption, but it was the middle of January, 1910, before all of the membranes had been again brought to their former sound condition. Profiting by the experience of 1909, the cells were left immersed in a *saturated* solution of thymol during the summer of 1910, and the bottles containing them were sealed up air-tight. The membranes were found to be in excellent condition in October. Unfortunately, however, a number of them were again infected in less than a month.

There is one observation which tends to confirm the idea that the *penicillium feeds* upon the membrane, which would, if correct, explain the ease with which the infection takes place and the destructive character of it. If a colony of *penicillium* and a quantity of ferrocyanide of copper are added to a solution of sugar, the red-brown ferrocyanide will visibly diminish within a short time and finally disappear, while the *penicillium* increases with great rapidity.

There is another observation which leads us to suspect that our membranes sometimes become infected with other things than *penicillium*. The small quantity of potassium ferrocyanide which is added to the sugar solutions imparts to them a slight but distinct color. In most instances, when the cell is opened, the color in question is found undiminished and unchanged, and the solution which is removed from the cell, after an experiment, cannot be distinguished from a reserved portion of the original solution. However, occasionally—but not often— the solution removed from the cell has a distinct *green* color, and some times a minute quantity of a greenish-blue solid is then found in the bottom of the cell. The phenomenon may recur several times in the same cell, but the course of treatment which is employed for *penicillium* also removes the cause of the green color, whatever it may be. The cells in which the green color appears do not develop the full normal pressure of the original solutions, and the contents of such cells are always found to have suffered some loss in rotation.

JOHNS HOPKINS UNIVERSITY,
March 1, 1911.

OBITUARY.

JULIUS WILHELM BRÜHL.

Prof. Julius Wilhelm Brühl died at Heidelberg February 5th, at the age of 61, having been born at Warsaw, February 13th, 1850. He began his college career at Zurich in 1868 and studied there and at Berlin for 5 years, thence going to Aachen, where he served several years as Landolt's assistant in the Polytechnikum. Here he began the work to which he devoted the greater part of his life, viz., the study of the refractivity of organic compounds. In 1875 he obtained his degree at Göttingen and four years later he was called to the Lemberg Technische Hochschule as professor of chemical technology. The unhealthiness of the climate forced him to resign his position there in 1884, and after spending some time at Freiburg he went, at Bunsen's solicitation, to Heidelberg as honorary professor at the Hochschule, taking over Bernthsen's private laboratory when the latter entered the employ of the Badische Anilin- und Soda-Fabrik. In 1889 he was lecturing at the University as Bunsen's representative and in 1908 was granted the full title of honorary professor. During this period (1896–1901), Volumes 5 to 9 of Roscoe and Schorlemmer's monumental treatise on organic chemistry were published under Brühl's supervision, with the coöperation of Hjelt and Aschan. His long and painstaking investigations on the relationship between the constitution and refractivity of organic compounds have been of incalculable use in solving problems of constitution which could not be cleared up by other means, and the refractometer is now an indispensible part of the equipment of every organic laboratory, not only where investigations of purely scientific interest are being carried out, but in technical establishments as well.

REVIEWS.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By A. F. HOLLEMAN, PH.D., F. R. A. AMST., Professor Ordinarius in the University of Amsterdam. Edited by A. JAMIESON WALKER, PH.D. (HEIDELBERG), B. A., Head of the Department of Chemistry, Technical College, Derby, England, assisted by OWEN E. MOTT, PH.D. (HEIDELBERG), with the coöperation of the author. Third English edition, partly rewritten. New York: John Wiley and Sons; London: Chapman and Hall, Ltd. 1910. pp. xx + 599. Price, $2.50.

The fact that Professor Holleman's book has gone through four editions in the original Dutch, seven in German, two in Russian, two in Italian, one in Polish and three in English, and that French and Japanese editions are in preparation is sufficient evidence of its popularity. In the preparation of the present from the second English edition, the chapter on the proteins has been rewritten and placed after the sugars, along with the amino acids, and the book has been brought up-to-date by many minor changes and additions and by the deletion of obsolete matter. While the reviewer cannot agree wholly with some of the statements made in the books (as, for example, on page 68, that the esterification of alcohols is a slow reaction because it takes place between molecules), yet, in clearness of presentation and in the judicial use of the more modern physical-chemical ideas as applied to organic chemistry, Prof. Holleman's book ranks among the best we have.

C. A. R.

Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge. Von Prof. Dr. P. Walden in Riga. Sammlung chemischer und chemisch-technischer Vorträge. Herausgegeben von Prof. Dr. W. Herz, Breslau. xv. Band, 8/12. Heft. Stuttgart. Verlag von Ferdinand Enke. 1910. pp. 181.

This is one of the most interesting and important books that has appeared in physical chemistry for some time. It is interesting because it is written in the live style which characterizes the publications of Walden, and important because it deals with thoroughness with one of the most important subjects in natural science.

The subject of solution is more wide-reaching and affects more branches of natural science than any other. Chemistry is essentially a science of solutions, and solution is fundamental to the biological sciences in general and to geology. Physical chemistry is connected with so many branches of science largely because it deals fundamentally with the nature of solutions. As the title implies, the whole subject of solution is discussed historically in this book, and sufficiently comprehensively for all practical purposes.

The first two chapters are devoted to the views of the ancients and the third to those held by those living in what may be termed the middle ages of science. The modern theories of solution, including the work of the last century, begin with Chapter IV, and are discussed in this and the remaining six chapters..

The whole discussion is characterized by scientific balance. It, however, seems to the reviewer that rather too much stress is laid upon the views of Pickering, but this is, after all, a matter of opinion.

The value of the work is greatly increased by copious references to the literature. H. C. J.

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CHEMICAL JOURNAL

A STUDY OF THE OPTICAL PROPERTIES OF SOME UNSATURATED KETONES.

BY FREDERICK H. GETMAN.

In a previous communication[1] we undertook the determination of some of the physical properties of unsaturated ketones and the investigation of the relation of these properties to their chemical behavior. In that paper the values of the surface tensions and densities of the following substances are recorded: mesityl oxide, benzalacetone, benzalmethylethyl ketone and benzalpinacolin.

It was shown by means of the well-known Eötvös-Ramsay relation and the empirical formula of Longinescu that these substances are nonassociated.

In the present paper the refractive indices, the dispersions and the absorption spectra of these compounds have been determined.

PART I.

Refraction and Dispersion.

The refractive indices were measured by means of the new form of Pulfrich refractometer,[2] using the *D* line of sodium and the *C*, *F*, and *G* lines of hydrogen. The temperature was controlled by means of the heating apparatus of Van Aubel, as made by Zeiss, and rarely varied more than one-tenth of a degree during the measurement. The mesityl oxide used

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[1] Getman: THIS JOURNAL, **44**, 145 (1910).

[2] Pulfrich: Z. physik. Chem., **18**, 294 (1895).

was obtained from Kahlbaum while the other substances were prepared in this laboratory and were subjected to repeated crystallization from low-boiling ligroin.

Owing to the tendency of these unsaturated compounds to become yellow on exposure to light and air, special precautions were taken to keep them in tightly-stoppered bottles in a dark place and to use them as soon as possible after preparation. That the refractive index changes on prolonged exposure was shown by the following experiment with mesityl oxide. The refractive index at 23°.5 of freshly distilled and nearly colorless mesityl oxide was found to be 1.44411, whereas the refractive index of the same specimen at the same temperature after seven weeks' exposure to diffuse light in a covered beaker was 1.44481. The mesityl oxide had acquired in this time a decided yellow color. The values of the refractive indices of the four compounds studied are given in the following tables, n_D, n_C, n_F, and n_G denoting the indices for the *D*, *C*, *F* and *G* lines.

Table I.—Mesityl Oxide, $(CH_3)_2C : CH.CO.CH_3$.

Temp.	n_D.	n_C.	n_F.	n_G.
13°	1.44840	1.44478	1.45831	1.46699
28°	1.44324	1.43768	1.45065	1.45970
29°	.....	1.43716	1.45035	1.45940
32°	1.43921	1.43599	1.44912	1.45794
38°	1.43658	1.43291	1.44594	1.45464
41°	1.43494	1.42951	1.44350	1.45314

Table II.—Benzalacetone, $C_6H_5CH : CH.CO.CH_3$.

Temp.	n_D.	n_C.	n_F.
33°.5	1.58929	1.58015	.....
36°.0	1.58870	1.57916	1.60356
39°.9	1.58674	1.57724	1.61266
44°.9	1.58411	1.57504	1.61023
47°.0	1.58314	1.57411	1.60902

Table III.—Benzalmethylethyl Ketone, $C_6H_5CH : CH.CO.C_2H_5$.

Temp.	n_D.	n_C.	n_F.
36°.0	1.57485	1.56621	.....
40°.0	1.57263	1.56450	1.59718
42°.1	1.57263	1.56950	1.59275
49°.1	1.56971	1.56072	1.59266
52°.0	1.56882	1.56025	1.60279

Table IV.— Benzalpinacolin, $C_6H_5CH : CH.CO.C(CH_3)_3$.

Temp.	n_D.	n_C.	n_F.
35°.2	1.55255	1.54469	1.57393
37°.1	1.55223	1.54396	1.57294
40°.0	1.55015	1.54270	1.57125
47°.5	1.54710	1.53952	1.56795
51°.9	1.54537	1.53771	1.56598

Benzalacetone, benzalmethylethyl ketone and benzalpinacolin show absorption in the violet so that it was impossible to secure trustworthy readings for the *G* line. It is to be noted that with these substances, which are solids at ordinary temperatures, several readings were taken on the supercooled liquids, but when the refractive indices are plotted against the temperatures no discontinuity is observed at the melting point. The melting points of the three substances are as follows:

	Melting point.
Benzalacetone	40°.2
Benzalmethylethyl ketone	37°.5
Benzalpinacolin	39°.5

Each index recorded in the tables is the mean of several observations and the corresponding temperature is the average of the initial and final temperatures.

The molecular refractions have been calculated by means of the Gladstone and Dale and the Lorentz-Lorenz formulas. In the subjoined tables *R* denotes the specific refraction obtained from the formula

$$R = \frac{n - 1}{d},$$

while *r* denotes the specific refraction calculated from the formula

$$r = \frac{1}{d} \cdot \frac{n^2 - 1}{n^2 + 2}.$$

The molecular weight is denoted by *M* while *d* denotes the density. The density was determined by means of a weight dilatometer, as previously described.

Table V.—Mesityl Oxide, $(CH_3)_2C:CH.CO.CH_3$.

Temp.	*d.*	MR_D.	Mr_D.	MR_C.	Mr_C.	MR_F.	Mr_F.	MR_G.	Mr_G.
13°	0.8672	50.67	30.21	50.25	30.28	51.79	30.84	52.76	31.37
28°	0.8525	50.95	30.46	50.31	30.16	51.70	30.94	52.84	31.49
29°	0.8519	.....	.....	50.28	30.14	51.81	30.91	52.84	31.44
32°	0.8500	50.64	30.33	50.26	30.14	51.78	30.93	52.80	31.47
38°	0.8430	50.75	30.45	50.32	30.18	51.83	31.01	52.85	31.52
41°	0.8405	50.72	30.41	50.08	30.11	51.71	30.96	52.83	31.53
	Mean,	50.77	30.37	50.25	30.17	51.77	30.77	52.82	31.47

Table VI.—Benzalacetone, $C_6H_5CH : CH.CO.CH_3$.

Temp.	*d.*	MR_D.	Mr_D.	MR_C.	Mr_C.	MR_F.	Mr_F.
33°.5	1.0142	84.83	48.53	83.51	47.96	...	...
36°.0	1.0124	84.88	48.63	83.53	47.98	87.04	49.64
39°.9	1.0095	84.86	48.62	83.48	47.90	88.61	50.30
44°.9	1.0060	84.77	48.57	83.46	47.96	88.55	50.34
47°.0	1.0043	84.77	48.72	83.46	47.98	88.53	50.43
	Mean,	84.82	48.61	83.49	47.96	88.56	50.18

Table VII.—Benzalmethylethyl Ketone, $C_6H_5CH : CH.CO.C_2H_5$.

Temp.	*d.*	MR_D.	Mr_D.	MR_C.	Mr_C.	MR_F.	Mr_F.
36°.0	0.9973	92.22	53.03	90.83	52.30	...	...
40°.0	0.9943	92.14	52.99	90.83	52.41	96.10	54.84
42°.1	0.9925	92.30	53.09	91.79	52.90	95.65	54.62
49°.1	0.9875	92.30	53.06	90.85	52.44	96.02	53.64
52°.0	0.9850	92.38	53.21	91.00	52.50	97.93	55.77
	Mean,	92.27	53.08	91.06	52.51	96.43	54.72

Table VIII.—Benzalpinacolin, $C_6H_5.CH : CH.CO.C(CH_3)_3$.

Temp.	*d.*	MR_D.	Mr_D.	MR_C.	Mr_C.	MR_F.	Mr_F.
35°.2	0.9584	108.34	62.75	106.84	61.97	112.57	64.71
37°.1	0.9570	108.48	62.73	106.86	62.00	112.56	64.73
40°.0	0.9548	108.33	62.69	106.86	62.20	112.48	64.71
47°.5	0.9490	108.37	62.82	106.88	62.13	112.52	64.79
51°.9	0.9455	108.42	62.85	106.92	62.16	112.54	64.86
	Mean,	108.39	62.77	106.87	62.09	112.53	64.76

The average molecular refractions calculated by means of the two formulas are compared with the molecular refractions computed from the refractivities of the elements as determined by Brühl and Conrady.[1] In these calculations the following values have been employed:

Table IX.

	Gladstone and Dale formula.		Lorentz-Lorenz formula.	
	R_C.	R_D.	r_C.	r_D.
Carbon, singly linked	5.00	4.71	2.365	2.592
Hydrogen	1.30	1.47	1.103	1.051
Oxygen, ketonic	3.40	3.33	2.328	2.287
Ethylene linkage	2.40	2.64	1.836	1.707

The agreement between the two sets of values is fairly close for mesityl oxide (Table X), but the remaining compounds all show marked optical anomaly. Brühl[2] has pointed out that optical anomaly is to be ascribed to the relative positions of unsaturated groups within the molecule. Where there is but one unsaturated group, as in mesityl oxide, the calculated and observed values of molecular refraction are in close agreement, but when the benzene nucleus is introduced into the molecule, as in benzalacetone, benzalmethylethyl ketone and benzalpinacolin, the molecular refractive power

Table X.

	Mesityl oxide.	Benzal-acetone.	Benzalmethyl-ethyl ketone.	Benzal-pinacolin.
MR_D obs.	50.77	84.82	92.27	108.39
MR_D calc.	48.93	75.69	83.34	98.64
Δ	1.84	9.13	8.93	9.75
Mr_D obs.	30.37	48.61	53.08	62.77
Mr_D calc.	29.51	44.64	49.24	58.44
Δ	0.86	3.97	3.84	4.33
MR_C obs.	50.25	83.49	91.06	106.87
MR_C calc.	48.80	76.00	83.60	98.80
Δ	1.45	7.49	7.46	8.07
Mr_C obs.	30.17	47.96	52.51	62.09
Mr_C calc.	29.38	44.35	48.92	58.07
Δ	0.79	3.61	3.59	4.02
Mr_F obs.	30.77	50.18	54.72	64.76
Mr_F calc.	30.09	45.28	49.96	59.33
Δ	0.68	4.90	4.76	5.43

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[1] Brühl: Z. physik. Chem., **7**, 191 (1891). Conrady: *Ibid.*, **3**, 210 (1889).

[2] Brühl: Ber. d. chem. Ges., **40**, 878, 1153 (1907); **41**, 3712 (1908).

becomes abnormal. An inspection of the results shows that in every case the molecular refraction is raised by the introduction of the second unsaturated group, the compounds exhibiting what has been termed "optical exaltation."[1] This abnormality in physical behavior is in perfect harmony with the chemical conduct of these compounds.

In 1886 Gladstone[2] suggested that the specific dispersive power of a substance might be represented by the expression $(n_H - n_A)/d$ and the molecular dispersion by $(n_H - n_A)M/d$, where M denotes the molecular weight and d the density. By comparing the molecular dispersions of a number of organic compounds he found that approximately constant values may be assigned to the dispersive power of hydrogen, carbon, oxygen and the halogens, thus proving dispersivity to be an additive property. Brühl[3] derived more exact values for the atomic dispersions and pointed out more definitely the relation between dispersive power and constitution. He employed the Lorentz-Lorenz relation for refractive power and calculated specific dispersions by means of the formula

$$\frac{n_x^2 - 1}{n_x^2 + 2} \cdot \frac{1}{d} - \frac{n_y^2 - 1}{n_y^2 + 2} \cdot \frac{1}{d}.$$

In calculating molecular dispersion (Table XIII) the following values of Brühl were employed:

Table XI.

	Atomic dispersion, $r_F - r_C$.
Carbon	0.039
Hydrogen	0.036
Ketonic oxygen	0.086
Ethylene linkage	0.230

The molecular dispersions for the C, D, F and G lines are given in Table XII and the observed and calculated values for the F and C lines are recorded in Table XIII. The differences between the observed and calculated molecular dispersions are in every case greater than the differences obtained by Brühl for saturated compounds.

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[1] Nasini: Gazz. chim. ital., **37**, II, 55 (1907).

[2] Gladstone: J. Chem. Soc., **50**, 609 (1886). P. Roy Soc., **42**, 401 (1887).

[3] Brühl: Z. physik. Chem., **7**, 140 (1891).

That there should be marked discrepancies between the two sets of values is not surprising, since it has been pointed out by Brühl that dispersive power is even more susceptible to differences in constitution than is refractivity.

Table XII.

	Mesityl oxide.	Benzal-acetone.	Benzalmethyl-ethyl ketone.	Benzal-pinacolin.
$MR_D—MR_C$	0.52	1.23	1.21	1.52
$Mr_D—Mr_C$	0.20	0.65	0.57	0.68
$MR_F—MR_C$	1.52	5.07	5.37	5.66
$Mr_F—Mr_C$	0.60	2.22	2.21	2.67
$MR_G—MR_C$	2.57	....	....	....
$Mr_G—Mr_C$	1.30	....	....	....

Table XIII.

	Mesityl oxide.	Benzal-acetone.	Benzalmethyl-ethyl ketone.	Benzal-pinacolin.
$Mr_F—Mr_C$ calc.	0.910	1.76	1.87	2.03
$Mr_F—Mr_C$ obs.	0.60	2.22	2.21	2.67
Δ	+0.31	—0.46	—0.34	—0.64

PART II.

Absorption Spectra.

The ultraviolet absorption spectra of benzalmethylethyl ketone and benzalpinacolin were obtained by means of a Fuess spectrograph fitted with a quartz prism and quartz lenses. The prism was set at the position of minimum deviation and the light from a rotating iron arc was focused upon the slit of the instrument by means of a quartz lens.

The ketones were dissolved in ethyl alcohol, the original solution being 0.0001 N. The solutions were contained in a Baly absorption tube[1] and placed before the slit of the spectrograph, the axis of the tube being coincident with the optical axis of the collimator.

After an exposure of fifteen seconds the length of the column of liquid was shortened, this being equivalent to diluting the solution, and a new exposure was made on a fresh portion of the plate.

The plates were measured by means of a comparator and the

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[1] Baly: Spectroscopy, p. 414.

results plotted according to the method of Baly and Desch.[1] The curves so obtained are shown in Fig. I, the dotted curve being

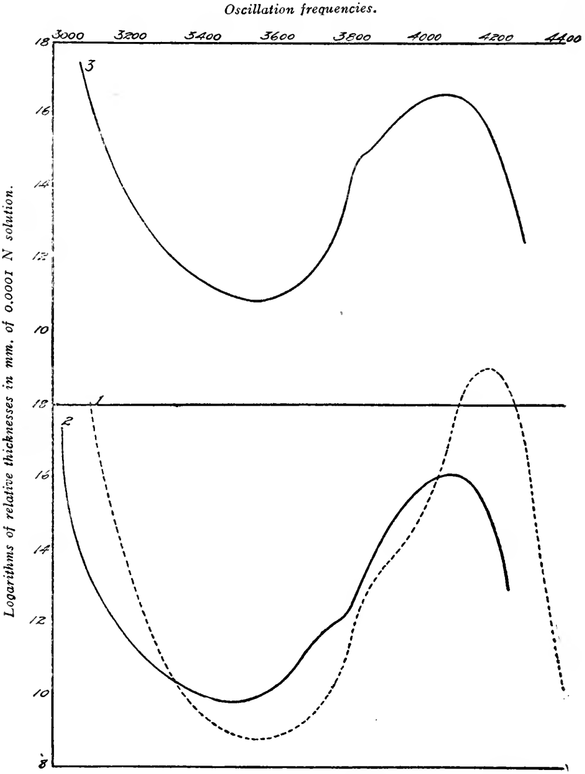

Fig. I.—1. Benzalacetone. 2. Benzalmethylethyl ketone. 3. Benzalpinacolin.

taken from the work of Baly and Schaefer.[2] The curves have the same general form, the heads of the bands being

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[1] Baly and Desch: J. Chem. Soc., **85,** 1039 (1904).

[2] Baly and Schaefer: *Ibid.*, **93,** 1813 (1908).

located in the vicinity of frequency 3500 and the persistence of the bands being nearly identical. Each curve is characterized by a slight sinuosity on the ascending portion. The similarity of the absorption curves is in agreement with the similarity of chemical behavior.

The preceding data on the ultraviolet absorption spectra of benzalmethylethyl ketone and benzalpinacolin were obtained by Miss Helen Lamberton, a former graduate student of this institution, and I desire to record my appreciation of her kindness in placing them at my disposal.

Bryn Mawr College,
Bryn Mawr, Pa.,
March, 1911.

ELECTRICAL INDUCTION IN CHEMICAL REACTIONS.

By L. G. Winston.

The object of this paper is to call attention to certain neglected aspects of chemical reaction, particularly the rôle which electrostatic induction may play. I mean, of course, by electrostatic induction the electrical attractions and repulsions of unlike and like charges, respectively. From the time of Berzelius, electrochemical theories have been advanced to explain chemical reaction, but in none of these is electrostatic induction properly taken into account.

This is difficult to explain, since the conditions demanded by the theories are just those which would give rise to inductive action. There are present ions carrying electrical charges, neutral undissociated molecules, and a nonconducting medium.

Sir J. J. Thomson's conception of the atom will be adopted in this discussion. According to him the atom consists of a sphere of positive electricity, through which are distributed the negative electrons. The whole is in a state of dynamical equilibrium.

An electron is either a small particle of matter carrying a unit negative charge of electricity, or simply a unit negative charge of electricity. We know practically nothing about the nature of positive electricity.

An atom that has lost an electron is electropositive.

An atom that has gained an electron is electronegative.

Chemical reactions are fundamentally connected with losses or gains in electrons.

With these ideas in mind, let us turn first to the consideration of one of the most characteristic reactions of carbon—the power to form homologous compounds.

Inorganic compounds are, in general, strongly dissociated. Here, chemical action is almost entirely ionic and induction plays little or no part.

Organic compounds, on the other hand, are weakly dissociated. Therefore, in solution we have only a few ions and a large number of undissociated molecules present.

Homology is effected by the substitution of a radical for a hydrogen atom. Objection has been made to some electrochemical theories in that in the formation of compounds such as ethane, either two similar groups (CH_3) having like charges must unite, or of necessity one methyl group must act positively and the other negatively. By means of the conception of the rôle played by induction this objection is, at least to some extent, removed.

In ordinary electrostatic induction in a conductor the following takes place. When a body charged, say positively, is brought near to a neutral body from which it is separated by a nonconducting medium, the electricities in the neutral body become separated. The negative is drawn nearest to the positive inducing body, while the positive is repelled. If, while the inducing body is still near, the repelled positive charge is removed, the once neutral body is left negatively charged.

Similarly, when positive methyl ions are brought into the presence of methane (or one of its substitution products in which one hydrogen atom has been replaced), ethane would be formed. The positive methyl group, approaching the neutral molecule of methane but separated from it by a nonconducting medium, would cause the electricities in the neutral molecule to separate.

We must, however, not think of the electricity as separating sharply into positive and negative—the positive of all the atoms accumulating in one-half of the molecule and the negative in the other. With Thomson's conception of the atom still in mind, we must think of the individual atoms within the molecule. The electrons within the atom, under the influence of the inducing body, still retain their same relative positions.

The inducing body merely draws nearer to itself the center of gravity of the negative electrons of each atom, repelling likewise the center of gravity of the positively charged part of each.

The inducing body, in drawing nearer to itself the electrons, draws one electron out of a hydrogen atom. Thus, one part of the molecule CH_4 gains an electron, becoming electronegative, and the hydrogen, losing an electron, becomes electropositive; the hydrogen, being positive, is repelled by the positive inducing body. The electrons, previously in a state of equilibrium, are now no longer in equilibrium. The repelled hydrogen ion will escape, if possible, and leave the molecule of methane (minus a hydrogen atom) charged negatively. The positive methyl group (the inducing body), being near, is attracted and finally drawn into the molecule.

In ordinary electrostatic induction, contact with a neutral body is necessary to remove the repelled charge, but here it is not necessary, since rapid motion of the molecule may cause its escape.

It is evident that in this way entire homologous series of carbon compounds could be built up.

Since the positive charge has never been found detached from a mass less than a hydrogen atom, and since we do not know fractions of atoms, in inductive action substitution will take place only when a charge equivalent to that of a hydrogen atom has been repelled from the neutral molecule.

Suppose, however, the inducing body has not power sufficient to expel a charge equivalent to that of a hydrogen ion, substitution cannot take place, but there will still be effects due to induction.

Suppose, for example, a molecule is so constituted that no hydrogen ion, or its equivalent, is free to escape from the molecule, but the only constituent free to move is an electron. While substitution does not take place, a state of strain would be set up; there would be a weakening or breaking of bonds due to the redistribution of atoms, necessitated by induction. Or, we may consider that there is a redistribution of atoms caused by the breaking of bonds. This might explain the tautomeric behavior of certain chemical compounds. Using the *enol-ketone* illustration,

$$\begin{array}{l}-\mathrm{CH}\\ \;\|\\ -\mathrm{COH}\end{array}\qquad\qquad\begin{array}{l}-\mathrm{CH_2}\\ \;|\\ -\mathrm{CO}\end{array},$$

Enol. Ketone.

inductive action, causing a rearrangement of the atoms within the molecule and the expulsion of an electron, might produce strain enough to break the double bond joining the two carbon atoms.

We see, on examination, that the rearrangement of the atoms is just such as would take place in the distribution of the two kinds of electricity in a neutral body by induction. The positive hydrogens all go to one carbon, while the negative oxygen remains attached to the other carbon. We find the same condition in the *lactime* form of tautomerism,

$$\begin{array}{l}-\mathrm{N}\\ \;\|\\ -\mathrm{COH}\end{array}\longrightarrow\begin{array}{l}-\mathrm{NH}\\ \;|\\ -\mathrm{CO}\end{array}.$$

The objection urged against the Berzelius electrochemical theory applies also to inductive action, viz., that hydrogen atoms are replaced by negative atoms. It is, however, well known that Sir J. J. Thomson, by brilliant experimental work, has overthrown this objection. We must, therefore, think of positively charged chlorine and negatively charged chlorine, positive methyl and negative methyl, etc. We can readily see that the effect produced in the molecule by a positively charged methyl group, acting as the inducing body, would be entirely different from that produced by a negatively charged methyl group.

The resultant molecule could be represented by the same chemical formula, but it is evident that the *arrangement* of atoms in the two would be different, giving rise to isomeric forms.

When we consider the close connection between isomerism, polarized light and electricity, knowing as we do that rotation of the beam of polarized light is dependent in some way upon a strain in the ether in the interior of the molecule, inductive action seems to be a condition under which such a strain and, consequently, the rotation of the beam of polarized light, might be produced.

Isomeric forms can, of course, be produced in other ways. For example, compounds formed by any of the following methods could have the same formulae:

(1) Polymerization of radicals having different charges.
(2) Interchange of ions, as in ordinary inorganic reactions.
(3) Substitution by means of inductive action.

Thus far we have dealt with saturated compounds. How do unsaturated differ from saturated compounds in their method of formation?

Suppose a body, *A*, charged with positive electricity, is separated by a nonconducting medium from a neutral body, *B*. The electricities in *B* become separated. If, while *A*, the charged body, is still present, the repelled charge in *B* is removed by contact or motion, *B* is left negatively charged. If *A* is near it may be drawn into *B* and *B* becomes neutral again. This happens in the case of saturated compounds.

If, on the other hand, *A*, the charged body, is too heavy or at too great a distance to be drawn into *B*, or if it moves away before it can be drawn into *B*, then *B* will remain a charged body, i. e., it becomes an unsaturated compound, and it will be able to form addition products; and this is characteristic of unsaturated compounds. These unsaturated molecules combining would also give rise to polymers.

The idea of induction seems to account for the variable valences of some of the elements, as will now be seen. Some elements, we have reason to believe, lose electrons more readily than others. These elements, having formed compounds, like other elements would be peculiarly sensitive to the inductive action of a charged ion. Electrons would be easily repelled from them, and they would again become capable of attaching other elements to themselves.

There is a limit, of course, to the number of electrons that could be repelled, since the loss of an electron would leave the molecule more strongly positive, which would tend to keep more electrons from escaping.

If this suggestion is true, the tendency to manifest different valences would be shown chiefly by the more electronegative elements, by those having a large atomic weight, and by those having small atomic volume. The reasons for the above are quite obvious. An electronegative element would be more likely to repel the negative electron. A large atomic weight probably means a large number of electrons, and the larger the number the more easily would some be lost. These conditions are quite strikingly illustrated in the elements manifesting different valences, such as chlorine, phosphorus, iodine, nitrogen, sulphur, oxygen, etc. In the curve produced by plotting atomic volumes as ordinates against atomic weights as abscissae, the very lowest points on the curve, those representing the smallest atomic volumes, are occupied by carbon, manganese, cobalt, nickel, copper, iron, and chromium. This seems quite significant in the light of the explanation just given.

Let us now attempt to apply this idea to catalysis.

The function of a catalyzer may be:

(1) To remove the repelled electricity, where the removal is essential to the electrification of the molecule, and consequent drawing in to itself of the radical or ion. A third body may be necessary here, as in the case of ordinary electrostatic induction, on account of the small velocity of the molecule.

(2) The catalyzer may serve to ionize one of the reagents and thus make the reaction continuous, which, for lack of ions, had been impossible.

(3) The catalyzer, dissociating, may by its charge help to draw the repelled charge (which cannot escape of itself) out of the molecule. It may render some bond easier to be broken, and thus make possible an entrance of an atom or group otherwise impossible.

(4) The charged body may not be near enough to the neutral body to bring about induction and, consequently, some carrier may be necessary.

(5) The charged body may be too heavy to be drawn into the neutral body without a carrier.

(6) The catalyzer may serve to break up an equilibrium which otherwise would exist.

(7) The catalyzer may tend to keep the undissociated molecule from dissociating.

The reaction may not be possible from mere union of differently charged ions—but entirely dependent on induction. In such case the molecule must be kept undissociated and neutral.

The fact that the conditions best suited to induction belong to organic chemistry, together with the fact that so many of the characteristics of organic compounds can be explained by the above suggestions, would seem to indicate that it is worthy of consideration.

It is true that difficulties arise in the application of induction to chemical reaction, but it undoubtedly helps to explain many things hitherto unexplained.

The foregoing presents but a bare outline of the part played by induction in chemical reaction.

Many other chemical phenomena can probably be explained by it. Among these are *steric hindrance*, and the fact that conductivity is not a true measure of dissociation in concentrated solutions, but a more detailed consideration of the subject will be given later.

Physical Chemical Laboratory,
Johns Hopkins University,
March, 1911.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

PART V.—THE MEASUREMENTS.

BY H. N. MORSE, W. W. HOLLAND, E. G. ZIES, C. N. MYERS, W. M. CLARK AND E. E. GILL.

The material for the measurements here presented was purified essentially by the method described by Cohen and Commelin.[2] One hundred and fifty pounds, approximately 70 kilograms, of the best "rock candy" were procured and subjected to the treatment which will be briefly described. Kilogram quantities of the sugar were dissolved, each in 500 cc. of boiled distilled water, which was warmed, but not allowed to rise above 60°. The solution (sometimes thinned with a little alcohol) was filtered, and from the filtrate the sugar was precipitated by alcohol which had been distilled from lime, a few crystals of the purest sugar being used to start the precipitation. The precipitated sugar was collected on a perforated porcelain disk in the bottom of a glass funnel. After removing all the mother liquor which could be drawn off by means of the filter pump, the material was transferred from the funnel to a porcelain dish and mixed to a thin paste with 85 per cent. alcohol. Finally, it was again filtered and then nearly dried by drawing through it filtered air. The original material and the product of the first precipitation will be designated hereafter by the letters *A* and *B*. The yield of *B* was about 32 kilograms.

The various portions of *B* were thoroughly mixed and then subjected to the treatment which has already been described, except that the precipitated material, after having been washed with diluted ethyl alcohol, was again washed in the same manner with warm methyl alcohol. The product, which will be designated by the letter *C*, amounted to about 16 kilograms.

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers upon this subject which have preceded the present one will be found in THIS JOURNAL, **26,** 80; **28,** 1; **29,** 137; **32,** 93; **34,** 1; **36,** 1 and 39; **37,** 324, 425 and 558; **38,** 175; **39,** 667; **40,** 1, 194, 266 and 325; **41,** 1, 92 and 557; **45,** 91, 237, 383, and 517.

[2] Z. physik. Chem., **64,** 1.

A portion of the sugar (*C*) which had been twice precipitated was again dissolved, reprecipitated, and washed with both ethyl and methyl alcohols. The product of the third precipitation will be designated by the letter *D*.

Combustions were made of all four products, namely *A*, the original rock candy; *B*, which had been precipitated once; *C*, twice; and *D*, three times. The results are given below in percentages of hydrogen and carbon.

	A.		*B.*		*C.*		*D.*	
	H	C	H	C	H	C	H	C
1	6.432	42.156	6.436	42.116	6.466	42.151	6.484	42.047
2	6.495	42.081	6.451	42.059	6.420	42.081	6.487	42.031
3	6.477	42.099	6.465	42.151	6.471	42.116	6.485	42.101
Mean	6.468	42.112	6.451	42.109	6.452	42.116	6.485	42.060
Theoret.	6.481	42.083	6.481	42.083	6.481	42.083	6.481	42.083
Dif.	—0.013	+0.029	—0.030	+0.026	—0.029	+0.033	—0.004	—0.023

The difference between the percentages of hydrogen and carbon which were found and the theoretical values are all within the unavoidable errors of analysis; and there is no reason to be found in the figures given above for believing one sample to be better than another. A determination of carbon and hydrogen does not, however, suffice for the detection of small quantities of glucose or invert sugar in cane sugar; and the probable presence of some reducing sugars could be detected in all of the samples. Much work was done in attempts to establish the limits within which these might be present. Finally, however, the whole question was referred to the National Bureau of Standards at Washington. The report which was received from the Bureau is given below:

Sample A.—Reducing substances in terms of invert sugar, 0.08 per cent. ±0.005 per cent.

Sample B.—Reducing substances in terms of invert sugar, 0.01 per cent. ±0.005 per cent.

Sample C.—Polarization, 99°.93. Reducing substances in terms of invert sugar, 0.01 per cent. ±0.005 per cent.

Sample D.—Polarization, 99°.95. Reducing substances in terms of invert sugar, 0.005, per cent. ±0.005 per cent.

The material which has been employed in the present investigation is that which is designated by the letter *C*, in which the Bureau of Standards found 0.01 per cent. of reducing sugar. The sample *D*, which had been recrystallized three times, is doubtless somewhat purer; but, as we have remarked elsewhere, *uniformity* of material is more important than absolute purity when a temperature coefficient is to be determined, and we feared that if the whole of the 16 kilograms of sample *C* were subjected to recrystallization, the product would not suffice for all of the work we had planned to do.

We have stated in a previous paper that, notwithstanding the extended investigation to which the manometers were subjected, we were not altogether satisfied with these instruments. It is to be said of them, however, that, as originally prepared for the investigation, they showed a high degree of concordance among themselves, which is all that is essential in determining a temperature coefficient. Toward the close of the work, three of the manometers (Numbers 11, 22 and 24) were opened and refilled with larger volumes of nitrogen with a view to diminishing the error of meniscus. As the gas now more than filled the calibrated portions of the tubes under ordinary pressure, it was necessary to determine its volume under increased pressure, and to use for this purpose the so-called "standard manometer" as a "side tube." It soon appeared, however, that we knew too little about the variations of capillary depression in the standard instrument. In other words, the volumes of the gas reduced to standard conditions appeared to vary somewhat according to the pressures under which they were determined. The refilled manometers were discarded after having been used in eight experiments, and, in order that there might be no uncertainty as to the results, the experiments in which they had been used were all repeated, at least twice, with other manometers which had not been refilled and which were known to be concordant among themselves.

For the first time, another membrane than copper ferrocyanide appears among the measurements of osmotic pressure.

Four of the determinations reported in this paper—Numbers XII, XIII, XV and XVIII—were made with membranes of nickel ferrocyanide. It was found long ago[1] that a considerable number of osmotically active membranes could be readily produced by the electrolytic process; but, though 25 of these have been made and tested qualitatively, we could not, until recently, spare the cells for the purpose of testing their suitability for quantitative work. The ferrocyanide of nickel appears to be superior in some respects to the corresponding salt of copper, but a comparison of the two will be withheld until a more thorough study of the former has been made.

Some of the experimental details which were given in the earlier communications in tabular form are omitted in this paper, because they can now be covered by general statements.

There was *no loss or gain in rotation* in any of the solutions whose pressures are reported, therefore none of the experiments are vitiated in consequence of leakage through the membranes. A number of the cells which were set up in the course of the investigation were found to be in a leaky condition—usually in consequence of infection which had escaped notice; but all experiments in which the slightest loss in concentration could be detected by the polariscope were rejected. Since the rotations of the solutions remained constant, it is clear that no *inversion* of the cane sugar occurred in the cells.

A solution sometimes *concentrates in the cell.* This happens whenever the solution is at a lower temperature than the bath at the time of filling and closing the cell. On being placed in the warmer bath, the solution expands, producing an over-pressure which forces some of the solvent outward through the membrane. Obviously, experiments in which such a concentration has taken place need not be rejected if one has the means of determining the precise amount of the concentration. Cells in which concentration has occurred give ultimately just as constant osmotic pressures as

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[1] THIS JOURNAL, **29**, 173.

those whose concentration has remained unchanged. *Concentration* of the kind described occurred in three instances in the course of the present investigation. The experiments are not included in this paper, though the results are valid and in perfect conformity with those which are reported. At moderate temperatures, e. g., below 40°, it is practicable to avoid a concentration of the kind described; for the cell may be filled, closed, and transferred to the bath without any sensible drop in the temperature of the solution. But at higher temperatures it is often necessary to determine the concentration of the solution whose pressure has been measured *after* the cell has been removed from the bath.

A solution may become *diluted* in a cell *without any leakage of the membrane,* and despite the fact that a mechanical pressure equal to the osmotic pressure is brought upon it at the time of closing the cell. This occurs when the solution at the time of filling the cell is at a higher temperature than that of the bath in which it is afterwards to stand. Such diluted solutions exhibit constant osmotic pressures, and the measurements are perfectly satisfactory if the exact degree of the dilution can be determined and *provided it can be demonstrated also that no part of the dilution was due to a break in the membrane which was afterwards effectually mended by the membrane formers.* The latter condition can rarely be fulfilled, hence it is safe to reject all experiments in which a dilution of the cell contents has occurred.

Especial attention is called to Experiment No. LXXIII, which was intended to serve as an *endurance* test of our membranes. The cell was not selected for this purpose because the membrane was supposed to be an unusually good one, but because at the time of setting up the cell we were able to spare the manometer and the bath for a long period of time. We have no reason for believing that any other cell employed in the 147 experiments to be reported would have made a less satisfactory record under the same conditions. The cell was set up on Jan. 24 with a 0.5 weight-normal solution at 15°. On Jan. 25 the mean osmotic pressure for the day was 12.522 atmospheres, the mean atmospheric pressure being 1.013. On March 25, the 60th day thereafter, the mean pressure for the day was also 12.522 atmospheres, the mean atmospheric pressure being 1.016. The lowest osmotic pressure observed during the entire two months was 12.517 atmospheres, while the highest was 12.552. The extreme (apparent) fluctuation in osmotic pressure was therefore 0.035 atmosphere. The extreme variation in atmospheric pressure during the same time was 1.0175 — 0.986 = 0.0315 atmosphere. In other words, the extreme (apparent) fluctuations in osmotic pressure were very nearly identical with those of the atmosphere. The highest osmotic pressures are contemporaneous with the lowest atmospheric pressures, and *vice versa*; and throughout the entire record, the fluctuations of osmotic and atmospheric pressures are of opposite signs. This is due, of course, to the fact that the pressure within the cell cannot instantaneously adjust itself to a change in atmospheric pressure, because the solvent *requires time* for its passage, inward or outward, through the membrane. It is for this reason that we regard it as probably more rational to employ mean values in correcting for atmospheric pressure. However, errors due to the opposite practice of correcting each observation for the atmospheric pressure prevailing at the time of reading tend to eliminate one another, so that the final mean osmotic pressure which is arrived at is probably very nearly correct, despite the fluctuations in atmospheric pressure. In the present case, the mean osmotic pressure for the 60 days is 12.5326 atmospheres, whichever method of correcting for atmospheric pressure is adopted. The apparent slight fluctuations in osmotic pressure are in reality only barometer effects. Thermometer effects played but a small part in this long-time experiment, for during the entire two months the temperature of the bath did not vary more than 0°.01.

On opening the cell on the 60th day, the rotation of the solution was found to be identical with that of the original one, showing that the solution had suffered no change in concentration, also that *no inversion of the cane sugar had occurred.*

The conduct of this cell, which maintained the concentration of its solution and a consequent osmotic pressure for more than eight weeks without the slightest evidence of approaching failure, proves, we think, first that our membranes are fulfilling their purpose in a satisfactory manner; and, secondly, that, under the conditions prevailing in our work, *the stirring of the solutions is unnecessary.* It appears to prove also that osmotically active membranes *may be made truly semipermeable*, a fact which is often denied, apparently on the basis of no better evidence than the fact that the products of most attempts at membrane-making are found to be leaky.

The whole subject of temperature maintenance during the present investigation can be covered in a few words. The temperature of the solutions did not vary during any experiment more than 0°.02. The usual fluctuations were certainly less than 0°.01. It is to be stated, however, by way of qualification, that in two or three instances a temporary drop in temperature exceeding 0°.02 occurred in consequence of accidents to the regulating devices, but in such cases the solutions were given ample time for recovery before the readings of the pressures were recorded. The thermometer effects throughout the entire work were very small. The fluctuations in pressure which will be noted in the following tables are, as in the case of Experiment LXXIII, already alluded to, principally barometer effects. The temperatures of the manometers (the "air space") were nearly equally satisfactory, except in the experiments at 0°, where the temperature of the space occupied by the gas-filled ends of these instruments was usually from 0°.1 to 0°.3 above 0°.

In Tables I to CXLVII, inclusive, there are given for each experiment: the concentration and temperature of the solution; the cell and the manometer which were used; the resistance of the membrane; the calculated gas pressure of the dissolved material at the same temperature if its volume were that of the solvent; the time of setting up the cell; and, finally, the osmotic pressures which were observed.

In Table CXLVIII, the results of the individual experiments are brought together, and there is given for each concentration and temperature: the osmotic pressure found;

the mean osmotic pressure; and the ratio of the mean to the calculated gas pressure.

Table CXLIX gives the mean osmotic pressure for each concentration and temperature; and Table CL, the ratio of these means to the calculated gas pressures.

Table I.

0.1 Wt. normal solution. Expt. 1 at 0°. Cell K_3. Resistance of membrane, 545,000 ohms. Manometer 13. Calc. gas pressure, 2.227 atms. Time of setting up cell, Mar. 8, 1909, 12.30 P.M. Initial pressure, 2.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 9, 10.00 A.M.	2.462	Mar. 9, 5.00 P.M.	2.460
2.00 P.M.	2.461	10, 12.30 P.M.	2.456
		Mean,	2.460

Table II.

0.1 Wt. normal solution. Expt. 2 at 0°. Cell K_3. Resistance of membrane, 224,000 ohms. Manometer 6. Calc. gas pressure, 2.227 atms. Time of setting up cell, April 12, 1909, 12.00 M. Initial pressure, 2.0 atms. Observed osmotic pressures:

	Atms.		Atms.
April 13, 10.00 A.M.	2.466	April 13, 9.30 A. M.	2.464
5.00 P.M.	2.465	14, 9.00 A. M.	2.460
		Mean,	2.464

Table III.

0.1 Wt. normal solution. Expt. 3 at 0°. Cell K_3. Resistance of membrane, 226,000 ohms. Manometer 6. Calc. gas pressure, 2.227 atms. Time of setting up cell, April 29, 1909, 3.00 P.M. Initial pressure, 2.3 atms. Observed osmotic pressures:

	Atms.		Atms.
April 30, 10.00 A.M.	2.465	April 30, 10.00 P.M.	2.460
5.00 P.M.	2.465	May 1, 10.00 A.M.	2.460
		Mean,	2.463
		Mean of experiments 1, 2 and 3,	2.462
		Ratio of osmotic to gas pressure,	1.106

Table IV.

0.1 Wt. normal solution. Expt. 1 at 5°. Cell K_3. Resistance of membrane, 366,000 ohms. Manometer 13. Calc. gas pressure, 2.267 atms. Time of setting up cell, Feb. 22, 1909, 3.00 P.M. Initial pressure, 2.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 23, 12.30 P.M.	2.455	Feb. 24, 9.00 A.M.	2.450
5.00 P.M.	2.455	1.00 P.M.	2.447
		Mean,	2.452

Table V.

0.1 Wt. normal solution. Expt. 2 at 5°. Cell L_3. Resistance of membrane, 550,000 ohms. Manometer 6. Calc. gas pressure, 2.267 atms. Time of setting up cell, Feb. 22, 1909, 3.00 P.M. Initial pressure, 2.39 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 23, 5.30 P.M.	2.453	Feb. 24, 10.00 A.M.	2.447
9.00 P.M.	2.452	2.00 P.M.	2.450
		Mean,	2.451

Table VI.

0.1 Wt. normal solution. Expt. 3 at 5°. Cell J_3. Resistance of membrane, 228,000 ohms. Manometer 13. Calc. gas pressure, 2.267 atms. Time of setting up cell, Feb. 25, 1909, 3.00 P.M. Initial pressure, 2.36 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 26, 10.00 A.M.	2.453	Feb. 27, 1.00 P.M.	2.456
4.30 P.M.	2.454	9.00 P.M.	2.448
		Mean,	2.453
		Mean of experiments 1, 2 and 3,	2.452
		Ratio of osmotic to gas pressure,	1.082

Table VII.

0.1 Wt. normal solution. Expt. 1 at 10°. Cell K_3. Resistance of membrane, 160,000 ohms. Manometer 13. Calc. gas pressure, 2.308 atms. Time of setting up cell, Mar. 1, 1909, 1.00 P.M. Initial pressure, 2.35 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 2, 9.00 A.M.	2.495	Mar. 2, 5.00 P.M.	2.493
1.00 P.M.	2.497	3, 9.00 A.M.	2.491
		Mean,	2.494

Table VIII.

0.1 Wt. normal solution. Expt. 2 at 10°. Cell N_3. Resistance of membrane, 133,000 ohms. Manometer 11. Calc. gas pressure, 2.308 atms. Time of setting up cell, Mar. 9, 1909, 12.30 P.M. Initial pressure, 2.40 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 9, 10.00 P.M.	2.500	Mar. 10, 12.30 P.M.	2.492
10, 10.00 A.M.	2.498	10.00 A.M.	2.494
		Mean,	2.496

Table IX.

0.1 Wt. normal solution. Expt. 3 at 10°. Cell O_3. Resistance of membrane, 151,000 ohms. Manometer 20. Calc. gas pressure, 2.308 atms. Time of setting up cell, Mar. 9, 1909, 12.30 P.M. Initial pressure, 2.43 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 9, 10.00 P.M.	2.492	Mar. 10, 4.00 P.M.	2.501
10, 10.00 A.M.	2.508	11, 9.30 A.M.	2.508
		Mean,	2.502

Table X.

0.1 Wt. normal solution. Expt. 4 at 10°. Cell J_3. Resistance of membrane, 176,000 ohms. Manometer 6. Calc. gas pressure, 2.308 atms. Time of setting up cell, Mar. 9, 1909, 12.30 P.M. Initial pressure, 2.41 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 10, 10.00 A.M.	2.503	Mar. 10, 4.00 P.M.	2.495
12.30 P.M.	2.498	10.00 P.M.	2.496
		Mean,	2.498
		Mean of experiments 1, 2, 3 and 4,	2.498
		Ratio of osmotic to gas pressure,	1.082

Table XI.

0.1 Wt. normal solution. Expt. 1 at 15°. Cell F_5. Resistance of the membrane, 225,000 ohms. Manometer 20. Calc. gas pressure, 2.349 atms. Time of setting up cell, Feb. 7, 1911, 2.00 P.M. Initial pressure, 2.4 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 11	2.551	Feb. 13	2.544
12	2.553	14	2.540
		Mean,	2.547

Table XII.

0.1 Wt. normal solution. Expt. 2 at 15°. Cell Ni–$_2$. Resistance of membrane,[1] 70,000 ohms. Manometer 9. Calc. gas pressure, 2.349 atms. Time of setting up cell, Jan. 13, 1911, 1.00 P.M. Initial pressure, 2.466 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 15	2.528	Jan. 17	2.538
16	2.538	18	2.535
		Mean,	2.535

Table XIII.

0.1 Wt. normal solution. Expt. 3 at 15°. Cell Ni–$_3$. Resistance of membrane,[1] 104,000 ohms. Manometer M$_1$. Calc. gas pressure, 2.349 atms. Time of setting up cell, Feb. 18, 1911, 12.00 M. Initial pressure, 2.315 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 19	2.544	Feb. 21	2.536
20	2.547	22	2.537
		Mean,	2.541

Table XIV.

0.1 Wt. normal solution. Expt. 4 at 15°. Cell Ni–$_2$. Resistance of membrane,[1] 112,000 ohms. Manometer 9. Calc. gas pressure, 2.349 atms. Time of setting up cell, Feb. 21, 1911, 3.00 P.M. Initial pressure, 2.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 22	2.532	Feb. 26	2.546
23	2.535	27	2.538
24	2.548	28	2.535
25	2.545	Mar. 1	2.530
		Mean,	2.538

Mean of experiments 1, 2, 3 and 4	2.540
Ratio of osmotic to gas pressure,	1.082

Table XV.

0.1 Wt. normal solution. Expt. 1 at 20°. Cell T$_3$. Resistance of membrane, 350,000 ohms. Manometer 9. Calc. gas pressure, 2.390 atms. Time of setting up cell, Mar. 7, 1910, 4.00 P.M. Initial pressure, 2.1 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 9, 9.00 A.M.	2.597	Mar. 9, 4.00 P.M.	2.579
12.30 P.M.	2.594	10, 9.00 A.M.	2.586
		Mean,	2.589

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[1] Nickel ferrocyanide.

Table XVI.

0.1 Wt. normal solution. Expt. 2 at 20°. Cell I_3. Resistance of membrane, 150,000 ohms. Manometer 15. Calc. gas pressure, 2.390 atms. Time of setting up cell, Mar. 7, 1910, 4.00 P.M. Initial pressure, 2.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 9, 9.00 A.M.	2.591	Mar. 10, 1.00 P.M.	2.589
10, 9.00 A.M.	2.589	5.00 P.M.	2.591
		Mean,	2.590

Mean of experiments 1 and 2, 2.590
Ratio of osmotic to gas pressure, 1.084

Table XVII.

0.1 Wt. normal solution. Expt. 1 at 25°. Cell T_3. Resistance of membrane, 367,000 ohms. Manometer 9. Calc. gas pressure, 2.431 atms. Time of setting up cell, Feb. 23, 1910, 4.00 P.M. Initial pressure, 2.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 26, 9.00 A.M.	2.631	Feb. 27, 10.00 A.M.	2.642
1.00 P.M.	2.633		
5.00 P.M.	2.634	Mean,	2.635

Table XVIII.

0.1 Wt. normal solution. Expt. 2 at 25°. Cell $\mathrm{Ni}-_2$. Resistance of membrane,[1] 65,000 ohms. Manometer 9. Calc. gas pressure, 2.431 atms. Time of setting up cell, Jan. 6, 1911, 2.00 P.M. Initial pressure, 2.639 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 7, 9.00 A.M.	2.639	Jan. 8, 9.00 A.M.	2.633
5.00 P.M.	2.620	10.00 A.M.	2.634
10.00 P.M.	2.627	8.00 P.M.	2.638
		Mean,	2.632

Mean of experiments 1 and 2, 2.634
Ratio of osmotic to gas pressure, 1.084

Table XIX.

0.2 Wt. normal solution. Expt. 1 at 0°. Cell Z_3. Resistance of membrane, 290,000 ohms. Manometer 5. Calc. gas pressure, 4.453 atms. Time of setting up cell, April 5, 1909, 3.00 P.M. Initial pressure, 4.6 atms. Observed osmotic pressures:

	Atms.		Atms.
April 6, 10.00 A.M.	4.721	April 7, 11.00 A.M.	4.719
5.00 P.M.	4.718		
10.00 P.M.	4.718	Mean,	4.719

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[1] Nickel ferrocyanide.

Table XX.

0.2 Wt. normal solution. Expt. 2 at 0°. Cell K_3. Resistance of membrane, 193,000 ohms. Manometer 6. Calc. gas pressure, 4.453 atms. Time of setting up cell, April 5, 1909, 3.00 P.M. Initial pressure, 4.5 atms. Observed osmotic pressures:

	Atms.		Atms.
April 6, 11.00 A.M.	4.712	April 7, 12.00 M.	4.720
5.00 P.M.	4.715		
10.00 P.M.	4.720	Mean,	4.717

Table XXI.

0.2 Wt. normal solution. Expt. 3 at 0°. Cell Q_2. Resistance of membrane, 220,000 ohms. Manometer 6. Calc. gas pressure, 4.453 atms. Time of setting up cell, April 14, 1909, 4.00 P.M. Initial pressure, 4.7 atms. Observed osmotic pressures:

	Atms.		Atms.
April 15, 10.00 A.M.	4.738	April 16, 10.00 A.M.	4.727
5.00 P.M.	4.729		
9.30 P.M.	4.725	Mean,	4.730

Table XXII.

0.2 Wt. normal solution. Expt. 4 at 0°. Cell M_3. Resistance of membrane, 278,000 ohms. Manometer 6. Calc. gas pressure, 4.453 atms. Time of setting up cell, April 16, 1909, 3.00 P.M. Initial pressure, 4.6 atms. Observed osmotic pressures:

	Atms.		Atms.
April 17, 10.30 A.M.	4.725	April 18, 5.00 P.M.	4.727
2.00 P.M.	4.727		
6.00 P.M.	4.725	Mean,	4.726
		Mean of experiments 1, 2, 3 and 4,	4.722
		Ratio of osmotic to gas pressure,	1.061

Table XXIII.

0.2 Wt. normal solution. Expt. 1 at 5°. Cell F_3. Resistance of membrane, 565,000 ohms. Manometer 6. Calc. gas pressure, 4.535 atms. Time of setting up cell, Jan. 25, 1909, 3.00 P.M. Initial pressure, 4.55 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 27, 9.00 A.M.	4.813	Jan. 28, 9.00 A.M.	4.812
11.00 P.M.	4.816	4.00 P.M.	4.807
		Mean,	4.812

Table XXIV.

0.2 Wt. normal solution. Expt. 2 at 5°. Cell J_3. Resistance of membrane, 270,000 ohms. Manometer 9. Calc. gas pressure, 4.535 atms. Time of setting up cell, Feb. 17, 1909, 12.00 M. Initial pressure, 4.7 atms. Observed osmotic pressures:

		Atms.			Atms.
Feb. 18,	9.00 A.M.	4.830	Feb. 19,	12.30 P.M.	4.820
	10.00 P.M.	4.825		5.00 P.M.	4.823
				Mean,	4.825
		Mean of experiments 1 and 2,			4.818
		Ratio of osmotic to gas pressure,			1.063

Table XXV.

0.2 Wt. normal solution. Expt. 1 at 10°. Cell H_3. Resistance of membrane, 100,000 ohms. Manometer 13. Calc. gas pressure, 4.616 atms. Time of setting up cell, Mar. 15, 1909, 12.30 P.M. Initial pressure, 4.73 atms. Observed osmotic pressures:

		Atms.			Atms.
Mar. 16,	9.00 A.M.	4.892	Mar. 17,	9.00 A.M.	4.889
	5.30 P.M.	4.892		2.00 P.M.	4.888
				Mean,	4.890

Table XXVI.

0.2 Wt. normal solution. Expt. 2 at 10°. Cell I_3. Resistance of membrane, 125,000 ohms. Manometer 20. Calc. gas pressure, 4.616 atms. Time of setting up cell, Mar. 15, 1909, 12.30 P.M. Initial pressure, 4.13 atms. Observed osmotic pressures:

		Atms.			Atms.
Mar. 16,	9.00 A.M.	4.901	Mar. 17,	9.00 A.M.	4.891
	5.00 P.M.	4.898			
	10.00 P.M.	4.895		Mean,	4.896
		Mean of experiments 1 and 2,			4.893
		Ratio of osmotic to gas pressure,			1.060

Table XXVII.

0.2 Wt. normal solution. Expt. 1 at 15°. Cell I_3. Resistance of membrane, 190,000 ohms. Manometer 6. Calc. gas pressure, 4.698 atms. Time of setting up cell, Feb. 2, 1911, 3.00 P.M. Initial pressure, 4.6 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 12	4.994	Feb 14	4.974
13	4.978	15	4.979
		Mean,	4.981

Table XXVIII.

0.2 Wt. normal solution. Expt. 2 at 15°. Cell R_3. Resistance of membrane, 550,000 ohms. Manometer 22. Calc. gas pressure, 4.698 atms. Time of setting up cell, Feb. 4, 1911, 10.00 A.M. Initial pressure, 5.03 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 16	5.003	Feb. 20	4.992
17	4.996	21	4.974
18	5.000	22	4.980
19	4.988	23	4.973
		Mean,	4.988
		Mean of experiments 1 and 2,	4.985
		Ratio of osmotic to gas pressure,	1.061

Table XXIX.

0.2 Wt. normal solution. Expt. 1 at 20°. Cell R_3. Resistance of membrane, 100,000 ohms. Manometer 20. Calc. gas pressure, 4.78 atms. Time of setting up cell, Mar. 12, 1910, 12.00 M. Initial pressure, 4.6 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 14, 10.00 A.M.	5.053	Mar. 15, 10.00 A.M.	5.052
1.00 P.M.	5.058		
5.00 P.M.	5.059	Mean,	5.056

Table XXX.

0.2 Wt. normal solution. Expt. 2 at 20°. Cell Q_3. Resistance of membrane, 180,000 ohms. Manometer 15. Calc. gas pressure, 4.78 atms. Time of setting up cell, Mar. 12, 1910, 12.00 M. Initial pressure, 4.8 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 15, 10.00 A.M.	5.066	Mar. 16, 1.00 P.M.	5.069
12.30 P.M.	5.068	10.00 P.M.	5.061
11.00 P.M.	5.067		
		Mean,	5.066

Table XXXI.

0.2 Wt. normal solution. Expt. 3 at 20°. Cell A_5. Resistance of membrane, 140,000 ohms. Manometer 9. Calc. gas pressure, 4.78 atms. Time of setting up cell, Dec. 15, 1910, 12.00 M. Initial pressure, 4.89 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 23	5.080	Dec. 29	5.062
24	5.086	30	5.058
25	5.071	31	5.035
26	5.060	Jan. 1	5.033
27	5.061	2	5.035
28	5.070	3	5.042
		Mean,	5.058

Table XXXII.

0.2 Wt. normal solution. Expt. 4 at 20°. Cell G_3. Resistance of membrane, 120,000 ohms. Manometer 24. Calc. gas pressure, 4.78 atms. Time of setting up cell, Dec. 22, 1910, 12.00 M. Initial pressure, 5.03 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 25	5.052	Dec. 28	5.065
26	5.080	29	5.060
27	5.078	30	5.054
		Mean,	5.065

Table XXXIII.

0.2 Wt. normal solution. Expt. 5 at 20°. Cell E_5. Resistance of membrane, 160,000 ohms. Manometer 15. Calc. gas pressure, 4.78 atms. Time of setting up cell, Dec. 22, 1910, 12.00 M. Initial pressure, 5.05 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 26	5.093	Dec. 31	5.061
27	5.079	Jan. 1	5.064
28	5.081	2	5.083
29	5.076	3	5.085
30	5.074		
		Mean,	5.074

Mean of experiments 1, 2, 3, 4 and 5, 5.064
Ratio of osmotic to gas pressure, 1.062

Table XXXIV.

0.2 Wt. normal solution. Expt. 1 at 25°. Cell A_4. Resistance of membrane, 560,000 ohms. Manometer 9. Calc. gas pressure, 4.862 atms. Time of setting up cell, Feb. 12, 1910, 12.00 M. Initial pressure, 4.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 13, 11.00 A.M.	5.160	Feb. 16, 5.00 P.M.	5.152
1.00 P.M.	5.152	2.00 P.M.	5.153
		Mean,	5.154

Table XXXV.

0.2 Wt. normal solution. Expt. 2 at 25°. Cell Q_3. Resistance of membrane, 180,000 ohms. Manometer 9. Calc. gas pressure, 4.862 atms. Time of setting up cell, Feb. 28, 1910, 12.00 M. Initial pressure, 4.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 3, 9.00 A.M.	5.142	Mar. 3, 4.30 P.M.	5.139
1.00 P.M.	5.143	10.00 P.M.	5.133
		Mean,	5.139

Table XXXVI.

0.2 Wt. normal solution. Expt. 3 at 25°. Cell M_3. Resistance of membrane, 535,000 ohms. Manometer 11. Calc. gas pressure, 4.862 atms. Time of setting up cell, Feb. 28, 1910, 12.00 M. Initial pressure, 4.7 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 1, 9.00 A.M.	5.162	Mar. 2, 9.00 A.M.	5.144
2.00 P.M.	5.157	9.00 P.M.	5.137
		Mean,	5.150
		Mean of experiments 1, 2 and 3,	5.148
		Ratio of osmotic to gas pressure,	1.059

Table XXXVII.

0.3 Wt. normal solution. Expt. 1 at 0°. Cell M_3. Resistance of membrane, 224,000 ohms. Manometer 11. Calc. gas pressure, 6.680 atms. Time of setting up cell, Mar. 15, 1909, 3.00 P.M. Initial pressure, 6.75 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 16, 2.00 P.M.	7.083	Mar. 17, 10.00 A.M.	7.073
10.00 P.M.	7.082	5.00 P.M.	7.074
		Mean,	7.078

Table XXXVIII.

0.3 Wt. normal solution. Expt. 2 at 0°. Cell M_3. Resistance of membrane, 224,000 ohms. Manometer 11. Calc. gas pressure, 6.680 atms. Time of setting up cell, April 2, 1909, 3.00 P.M. Initial pressure, 7.0 atms. Observed osmotic pressures:

		Atms.			Atms.
April 3,	1.00 P.M.	7.113	April 4,	6.00 P.M.	7.107
4,	12.00 M.	7.105	5,	10.00 A.M.	7.102
				Mean,	7.107

Table XXXIX.

0.3 Wt. normal solution. Expt. 3 at 0°. Cell M_3. Resistance of membrane, 185,000 ohms. Manometer 6. Calc. gas pressure, 6.680 atms. Time of setting up cell, April 20, 1909, 3.00 P.M. Initial pressure, 7.00 atms. Observed osmotic pressures:

		Atms.			Atms.
April 21,	5.00 P.M.	7.067	April 22,	10.00 A.M.	7.073
	10.30 P.M.	7.068		2.00 P.M.	7.074
				Mean,	7.071

Mean of experiments 1, 2 and 3, 7.085
Ratio of osmotic to gas pressure, 1.061

Table XL.

0.3 Wt. normal solution. Expt. 1 at 5°. Cell J_3. Resistance of membrane, 366,000 ohms. Manometer 6. Calc. gas pressure, 6.862 atms. Time of setting up cell, Jan. 28, 1909, 3.30 P.M. Initial pressure, 5.66 atms. Observed osmotic pressures:

		Atms.			Atms.
Jan. 29,	5.00 P.M.	7.190	Jan. 30,	10.00 A.M.	7.187
	11.00 P.M.	7.187		1.00 P.M.	7.185
				Mean,	7.187

Table XLI.

0.3 Wt. normal solution. Expt. 2 at 5°. Cell K_3. Resistance of membrane, 224,000 ohms. Manometer 9. Calc. gas pressure, 6.802 atms. Time of setting up cell, Feb. 13, 1909, 12.30 P.M. Initial pressure, 6.89 atms. Observed osmotic pressures:

		Atms.			Atms.
Feb. 15,	12.30 P.M.	7.219	Feb. 15,	11.00 P.M.	7.209
	5.00 P.M.	7.212	" 16,	12.00 M.	7.195
				Mean,	7.209

Mean of experiments 1 and 2, 7.198
Ratio of osmotic to gas pressure, 1.058

Table XLII.

0.3 Wt. normal solution. Expt. 1 at 10°. Cell F_5. Resistance of membrane, 150,000 ohms. Manometer M_1. Calc. gas pressure, 6.925 atms. Time of setting up cell, Jan. 26, 1911, 3.00 P.M. Initial pressure, 8.0 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 30	7·325	Feb. 1	7·347
31	7·319	2	7·337
		Mean,	7·332

Table XLIII.

0.3 Wt. normal solution. Expt. 2 at 10°. Cell E_5. Resistance of membrane, 220,000 ohms. Manometer 9. Calc. gas pressure, 6.925 atms. Time of setting up cell, Jan. 26, 1911, 3.00 P.M. Initial pressure, 7.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 30	7·324	Feb. 1	7·346
31	7·353	2	7·324
		Mean,	7·337

Mean of experiments 1 and 2,	7·334
Ratio of osmotic to gas pressure,	1.059

Table XLIV.

0.3 Wt. normal solution. Expt. 1 at 15°. Cell C_5. Resistance of membrane, 230,000 ohms. Manometer 6. Calc. gas pressure, 7.047 atms. Time of setting up cell, Jan. 16, 1911, 3.00 P.M. Initial pressure, 7.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 19	7·465	Jan. 21	7·466
20	7·463		
		Mean,	7·465

Table XLV.

0.3 Wt. normal solution. Expt. 2 at 15°. Cell T_3. Resistance of membrane, 110,000 ohms. Manometer M_1. Calc. gas pressure, 7.047 atms. Time of setting up cell, Feb. 2, 1911, 3.00 P.M. Initial pressure, 7.68 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 8	7·481	Feb. 10	7·498
9	7·498	11	7·465
		Mean,	7·486

Mean of experiments 1 and 2,	7·476
Ratio of osmotic to gas pressure,	1.061

Table XLVI.

0.3 Wt. normal solution. Expt. 1 at 20°. Cell I_3. Resistance of membrane, 214,000 ohms. Manometer 20. Calc. gas pressure, 7.17 atms. Time of setting up cell, Mar. 15, 1910, 11.00 A.M. Initial pressure, 7.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 16, 11.00 A.M.	7.570	Mar. 17, 11.00 P.M.	7.582
17, 1.00 P.M.	7.590	18, 9.00 P.M.	7.600
		Mean,	7.586

Table XLVII.

0.3 Wt. normal solution. Expt. 2 at 20°. Cell T_3. Resistance of membrane, 535,000 ohms. Manometer 9. Calc. gas pressure, 7.17 atms. Time of setting up cell, Mar. 15, 1910, 11.00 A.M. Initial pressure, 7.8 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 17, 10.00 A.M.	7.642	Mar. 18, 5.00 P.M.	7.618
5.00 P.M.	7.610	19, 9.00 P.M.	7.627
		Mean,	7.624

Table XLVIII.

0.3 Wt. normal solution. Expt. 3 at 20°. Cell M_3. Resistance of membrane, 270,000 ohms. Manometer 24. Calc. gas pressure, 7.17 atms. Time of setting up cell, Dec. 12, 1910, 2.00 P.M. Initial pressure, 7.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 16	7.629	Dec. 18	7.596
17	7.589	19	7.609
		Mean,	7.606
		Mean of experiments 1, 2 and 3,	7.605
		Ratio of osmotic to gas pressure,	1.060

Table XLIX.

0.3 Wt. normal solution. Expt. 1 at 25°. Cell K_3. Resistance of membrane, 280,000 ohms. Manometer 20. Calc. gas pressure, 7.292 atms. Time of setting up cell, Jan. 31, 1910, 12.00 M. Initial pressure, 7.15 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 1, 1.00 P.M.	7.728	Feb. 2, 5.00 P.M.	7.738
5.00 P.M.	7.734	10.00 P.M.	7.741
		Mean,	7.735

Table L.

0.3 Wt. normal solution. Expt. 2 at 25°. Cell R_3. Resistance of membrane, 92,000 ohms. Manometer 20. Calc. gas. pressure, 7.292 atms. Time of setting up cell, Mar. 2, 1910, 4.00 P.M. Initial pressure, 6.9 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 4, 1.00 P.M.	7.727	Mar. 5, 9.00 A.M.	7.703
5.00 P.M.	7.735	2.30 P.M.	7.712
		Mean,	7.719

Table LI.

0.3 Wt. normal solution. Expt. 3 at 25°. Cell C_5. Resistance of membrane, 200,000 ohms. Manometer 6. Calc. gas pressure, 7.292 atms. Time of setting up cell, Nov. 2, 1910, 1.00 P.M. Initial pressure, 7.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 3, 4.00 P.M.	7.725	Nov. 4, 11.00 P.M.	7.720
4, 9.00 A.M.	7.730	5, 9.00 A.M.	7.715
3.00 P.M.	7.720		
		Mean,	7.722

Table LII.

0.3 Wt. normal solution. Expt. 4 at 25°. Cell D_5. Resistance of membrane, 190,000 ohms. Manometer 9. Calc. gas pressure, 7.292 atms. Time of setting up cell, Nov. 2, 1910, 1.00 P.M. Initial pressure, 6.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 4	7.740	Nov. 6	7.732
5	7.732	7	7.742
		Mean,	7.738
		Mean of experiments 1, 2, 3 and 4,	7.729
		Ratio of osmotic to gas pressure,	1.060

Table LIII.

0.4 Wt. normal solution. Expt. 1 at 0°. Cell D_3. Resistance of membrane, 236,000 ohms. Manometer 13. Calc. gas pressure, 8.906 atms. Time of setting up cell, Feb. 2, 1909, 12.00 M. Initial pressure, 9.51 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 3, 12.00 M.	9.436	Feb. 4, 9.00 A.M.	9.462
5.00 P.M.	9.443	2.00 P.M.	9.458
		Mean,	9.450

Table LIV.

0.4 Wt. normal solution. Expt. 2 at 0°. Cell E_3. Resistance of membrane, 183,000 ohms. Manometer 6. Calc. gas pressure, 8.906 atms. Time of setting up cell, Mar. 27, 1909, 2.00 P.M. Initial pressure, 9.1 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 28, 11.00 A.M.	9.425	Mar. 29, 12.00 M.	9.440
29, 10.00 A.M.	9.434	3.00 P.M.	9.440
		Mean,	9.435
		Mean of experiments 1 and 2,	9.442
		Ratio of osmotic to gas pressure,	1.060

Table LV.

0.4 Wt. normal solution. Experiment 1 at 5°. Cell F_3. Resistance of membrane, 550,000 ohms. Manometer 13. Calc. gas pressure, 9.07 atms. Time of setting up cell, Jan. 30, 1909, 12.00 M. Initial pressure, 7.27 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 1, 9.30 A.M.	9.622	Feb. 1, 10.00 P.M.	9.623
1.00 P.M.	9.622	2, 9.00 A.M.	9.625
		Mean,	9.623

Table LVI.

0.4 Wt. normal solution. Expt. 2 at 5°. Cell E_3. Resistance of membrane, 550,000 ohms. Manometer 22. Calc. gas pressure, 9.07 atms. Time of setting up cell, Jan. 30, 1909, 12.00 M. Initial pressure, 8.79 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 31, 11.30 A.M.	9.596	Feb. 1, 1.00 P.M.	9.576
5.00 P.M.	9.586	4.00 P.M.	9.578
		Mean,	9.584

Table LVII.

0.4 Wt. normal solution. Expt. 3 at 5°. Cell K_3. Resistance of membrane, 550,000 ohms. Manometer 9. Calc. gas pressure, 9.07 atms. Time of setting up cell, Jan. 30, 1909, 12.00 M. Initial pressure, 9.28 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 30, 10.30 P.M.	9.644	Jan. 31, 5.30 P.M.	9.623
31, 11.30 A.M.	9.631	Feb. 1, 4.00 P.M.	9.571
		Mean,	9.617
		Mean of experiments 1, 2 and 3,	9.608
		Ratio of osmotic to gas pressure,	1.059

Table LVIII.

0.4 Wt. normal solution. Expt. 1 at 10°. Cell D_3. Resistance of membrane, 160,000 ohms. Manometer 21. Calc. gas pressure, 9.233 atms. Time of setting up cell, April 16, 1909, 12.30 P.M. Initial pressure, 8.76 atms. Observed osmotic pressures:

	Atms.		Atms.
April 17, 1.30 P.M.	9.786	April 18, 5.00 P.M.	9.795
9.30 P.M.	9.789	19, 9.00 A.M.	9.792
		Mean,	9.791

Table LIX.

0.4 Wt. normal solution. Expt. 2 at 10°. Cell O_3. Resistance of membrane, 150,000 ohms. Manometer 9. Calc. gas pressure, 9.233 atms. Time of setting up cell, April 19, 1909, 3.00 P.M. Initial pressure, 9.38 atms. Observed osmotic pressures:

	Atms.		Atms.
April 20, 3.00 P.M.	9.789	April 21, 1.00 P.M.	9.792
21, 11.00 A.M.	9.787	4.00 P.M.	9.793
		Mean,	9.790

Mean of experiments 1 and 2, 9.790
Ratio of osmotic to gas pressure, 1.060

Table LX.

0.4 Wt. normal solution. Expt. 1 at 15°. Cell M_3. Resistance of membrane, 150,000 ohms. Manometer 24. Calc. gas pressure, 9.396 atms. Time of setting up cell, Jan. 9, 1911, 1.00 P.M. Initial pressure, 9.92 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 12	9.920	Jan. 14	9.979
13	9.952	15	9.949
		Mean,	9.950

Table LXI.

0.4 Wt. normal solution. Expt. 2 at 15°. Cell N_3. Resistance of membrane, 160,000 ohms. Manometer 6. Calc. gas pressure, 9.396 atms. Time of setting up cell, Jan. 9, 1911, 1.00 P.M. Initial pressure, 9.86 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 11	9.937	Jan. 13	9.971
12	9.947	14	9.931
		Mean,	9.947

Mean of experiments 1 and 2, 9.949
Ratio of osmotic to gas pressure, 1.059

Table LXII.

0.4 Wt. normal solution. Expt. 1 at 20°. Cell G_3. Resistance of membrane, 110,000 ohms. Manometer 9. Calc. gas pressure, 9.56 atms. Time of setting up cell, Mar. 19, 1910, 1.00 P.M. Initial pressure, 10.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 20, 10.00 A.M.	10.138	Mar. 21, 9.00 P.M.	10.137
21, 4.00 P.M.	10.148	22, 1.00 P.M.	10.121
		Mean,	10.136

Table LXIII.

0.4 Wt. normal solution. Expt. 2 at 20°. Cell I_3. Resistance of membrane, 285,000 ohms. Manometer 9. Calc. gas pressure, 9.56 atms. Time of setting up cell, Mar. 23, 1910, 3.00 P.M. Initial pressure, 10.4 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 26, 1.00 P.M.	10.161	Mar. 26, 11.00 P.M.	10.125
5.00 P.M.	10.135	28, 11.00 A.M.	10.129
		Mean,	10.138

Mean of experiments 1 and 2,	10.137
Ratio of osmotic to gas pressure,	1.060

Table LXIV.

0.4 Wt. normal solution. Expt. 1 at 25°. Cell Q_3. Resistance of membrane, 540,000 ohms. Manometer 9. Calc. gas pressure, 9.723 atms. Time of setting up cell, Dec. 1, 1909, 4.00 P.M. Initial pressure, 10.129 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 2	10.305	Dec. 4	10.292
3	10.305		
		Mean,	10.298

Table LXV.

0.4 Wt. normal solution. Expt. 2 at 25°. Cell T_3. Resistance of membrane, 357,000 ohms. Manometer 9. Calc. gas pressure, 9.723 atms. Time of setting up cell, Dec. 6, 1909, 5.00 P.M. Initial pressure, 10.910 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 7, 4.00 P.M.	10.298	Dec. 8, 5.00 P.M.	10.312
8, 11.00 A.M.	10.285	9, 4.00 P.M.	10.285
		Mean,	10.295

Mean of experiments 1 and 2,	10.296
Ratio of osmotic to gas pressure,	1.059

Table LXVI.

0.5 Wt. normal solution. Expt. 1 at 0°. Cell M_2. Resistance of membrane, 160,000 ohms. Manometer 11. Calc. gas pressure, 11.133 atms. Time of setting up cell, April 9, 1909, 3.00 P.M. Initial pressure, 11.8 atms. Observed osmotic pressures:

	Atms.		Atms.
April 10, 9.00 A.M.	11.915	April 11, 11.00 A.M.	11.912
1.00 P.M.	11.912	12, 10.00 A.M.	11.890
		Mean,	11.907

Table LXVII.

0.5 Wt. normal solution. Expt. 2 at 0°. Cell E_3. Resistance of membrane, 140,000 ohms. Manometer 6. Calc. gas pressure, 11.133 atms. Time of setting up cell, April 9, 1909, 3.00 P.M. Initial pressure, 11.7 atms. Observed osmotic pressures:

	Atms.		Atms.
April 10, 1.00 P.M.	11.862	April 11, 5.00 P.M.	11.884
9.00 P.M.	11.869	12, 10.00 A.M.	11.912
		Mean,	11.882
		Mean of experiments 1 and 2,	11.895
		Ratio of osmotic to gas pressure,	1.068

Table LXVIII.

0.5 Wt. normal solution. Expt. 1 at 5°. Cell H_3. Resistance of membrane, 500,000 ohms. Manometer 9. Calc. gas pressure, 11.34 atms. Time of setting up cell, Jan. 21, 1909, 3.00 P.M. Initial pressure, 12.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 22, 4.30 A.M.	12.10	Jan. 22, 1.00 P.M.	12.10
9.00 A.M.	12.12	11.00 P.M.	12.08
		Mean,	12.10

Table LXIX.

0.5 Wt. normal solution. Expt. 2 at 5°. Cell E_3. Resistance of membrane, 550,000 ohms. Manometer 13. Calc. gas pressure, 11.34 atms. Time of setting up cell, Jan. 22, 1909, 3.30 P.M. Initial pressure, 10.74 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 23, 3.00 A.M.	12.09	Jan. 24, 5.00 P.M.	12.10
2.30 P.M.	12.10	25, 9.00 A.M.	12.09
		Mean,	12.10
		Mean of experiments 1 and 2,	12.10
		Ratio of osmotic to gas pressure,	1.067

Table LXX.

0.5 Wt. normal solution. Expt. 1 at 10°. Cell J_3. Resistance of membrane, 140,000 ohms. Manometer 24. Calc. gas pressure, 11.541 atms. Time of setting up cell, April 12, 1909, 11.00 A.M. Initial pressure, 12.91 atms. Observed osmotic pressures:

	Atms.		Atms.
April 13, 5.00 P.M.	12.289	April 14, 10.00 P.M.	12.298
14, 1.00 P.M.	12.298	15, 10.00 P.M.	12.298
		Mean,	12.296

Table LXXI.

0.5 Wt. normal solution. Expt. 2 at 10°. Cell F_3. Resistance of membrane, 181,000 ohms. Manometer 15. Calc. gas pressure, 11.541 atms. Time of setting up cell, April 12, 1909, 11.00 A.M. Initial pressure, 10.67 atms. Observed osmotic pressures:

	Atms.		Atms.
April 14, 9.00 A.M.	12.299	April 14, 10.00 P.M.	12.302
1.00 P.M.	12.297	15, 10.00 A.M.	12.292
		Mean,	12.298
		Mean of experiments 1 and 2,	12.297
		Ratio of osmotic to gas pressure,	1.066

Table LXXII.

0.5 Wt. normal solution. Expt. 1 at 15°. Cell F_5. Resistance of membrane, 160,000 ohms. Manometer 15. Calc. gas pressure, 11.745 atms. Time of setting up cell, Jan. 5, 1911, 3.00 P.M. Initial pressure, 12.563 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 7	12.563	Jan. 10	12.558
8	12.575	11	12.566
9	12.565		
		Mean,	12.565

Table LXXIII.

0.5 Wt. normal solution. Expt. 2 at 15°. Cell C_5. Resistance of membrane, 100,000 ohms. Manometer 24. Calc. gas pressure, 11.745 atms. Time of setting up cell, Jan. 24, 1911, 12.00 M. Initial pressure, 12.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 25	12.522	Feb. 24	12.537
26	12.535	25	12.531
27	12.544	26	12.536
28	12.534	27	12.533
29	12.536	28	12.532
30	12.552	Mar. 1	12.537
31	12.535	2	12.517
Feb. 1	12.536	3	12.517
2	12.538	4	12.524
3	12.524	5	12.529
4	12.541	6	12.533
5	12.537	7	12.523
6	12.529	8	12.528
7	12.532	9	12.530
8	12.531	10	12.546
9	12.539	11	12.534
10	12.533	12	12.544
11	12.527	13	12.533
12	12.530	14	12.532
13	12.527	15	12.552
14	12.536	16	12.533
15	12.525	17	12.532
16	12.526	18	12.535
17	12.536	19	12.533
18	12.534	20	12.540
19	12.524	21	12.536
20	12.537	22	12.545
21	12.524	23	12.539
22	12.535	24	12.527
23	12.535	25	12.522

Mean, 12.5326
Ratio of osmotic to gas pressure, 1.067
Mean of experiments 1 and 2, 12.5488
Ratio of osmotic to gas pressure, 1.068

Table LXXIV.

0.5 Wt. normal solution. Expt. 1 at 20°. Cell G_3. Resistance of membrane, 367,000 ohms. Manometer 15. Calc. gas pressure, 11.95 atms. Time of setting up cell, Jan. 20, 1910, 3.00 P.M. Initial pressure, 11.50 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 20, 9.30 P.M.	12.741	Jan. 21, 9.30 P.M.	12.738
21, 9.00 A.M.	12.754	22, 10.00 P.M.	12.735
		Mean,	12.742

Table LXXV.

0.5 Wt. normal solution. Expt. 2 at 20°. Cell R_3. Resistance of membrane, 162,000 ohms. Manometer 15. Calc. gas pressure, 11.95 atms. Time of setting up cell, Mar. 21, 1910, 2.00 P.M. Initial pressure, 12.55 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 22, 1.00 P.M.	12.753	Mar. 23, 9.00 A.M.	12.757
9.00 P.M.	12.763	24, 9.00 A.M.	12.742
		Mean,	12.754
		Mean of experiments 1 and 2,	12.748
		Ratio of osmotic to gas pressure,	1.067

Table LXXVI.

0.5 Wt. normal solution. Expt. 1 at 25°. Cell W_3. Resistance of membrane, 275,000 ohms. Manometer 9. Calc. gas pressure, 12.154 atms. Time of setting up cell, Oct. 19, 1909, 4.30 P.M. Initial pressure, 13.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Oct. 20, 9.00 A.M.	12.871	Oct. 21, 5.00 P.M.	12.920
20, 10.00 P.M.	12.948	22, 9.00 A.M.	12.918
21, 9.00 A.M.	12.937		
		Mean,	12.919

Table LXXVII.

0.5 Wt. normal solution. Expt. 2 at 25°. Cell T_3. Resistance of membrane, 285,000 ohms. Manometer 9. Calc. gas pressure, 12.154 atms. Time of setting up cell, Oct. 29, 1909, 4.30 P.M. Initial pressure, 12.51 atms. Observed osmotic pressures:

	Atms.		Atms.
Oct. 30, 9.00 A.M.	12.997	Nov. 1, 10.00 A.M.	12.915
31, 11.00 A.M.	12.991	1.00 P.M.	12.915
9.30 P.M.	12.918		
		Mean,	12.947

Table LXXVIII.

0.5 Wt. normal solution. Expt. 3 at 25°. Cell Q_3. Resistance of membrane, 220,000 ohms. Manometer 11. Calc. gas pressure, 12.154 atms. Time of setting up cell, Nov. 11, 1909, 5.00 P.M. Initial pressure, 12.74 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 12, 2.00 P.M.	12.912	Nov. 13, 1.00 P.M.	12.948
5.00 P.M.	12.912	9.30 P.M.	12.954
		Mean,	12.932

Table LXXIX.

0.5 Wt. normal solution. Expt. 4 at 25°. Cell T_3. Resistance of membrane, 370,000 ohms. Manometer 9. Calc. gas pressure, 12.154 atms. Time of setting up cell, Nov. 11, 1909, 5.00 P.M. Initial pressure, 11.32 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 12, 10.00 A.M.	12.963	Nov. 12, 11.00 P.M.	12.989
5.00 P.M.	13.001	13, 9.30 P.M.	12.935
		Mean,	12.972
		Mean of experiments 1, 2, 3 and 4,	12.943
		Ratio of osmotic to gas pressure,	1.065

Table LXXX.

0.6 Wt. normal solution. Expt. 1 at 0°. Cell E_3. Resistance of membrane, 151,000 ohms. Manometer 6. Calc. gas pressure, 13.359 atms. Time of setting up cell, Mar. 18, 1909, 3.00 P.M. Initial pressure, 14.02 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 19, 12.00 M.	14.364	Mar. 20, 2.00 P.M.	14.373
11.30 P.M.	14.363	5.00 P.M.	14.367
		Mean,	14.367

Table LXXXI.

0.6 Wt. normal solution. Expt. 2 at 0°. Cell Q_3. Resistance of membrane, 212,000 ohms. Manometer 11. Calc. gas pressure, 13.359 atms. Time of setting up cell, April 7, 1909, 3.00 P.M. Initial pressure, 14.3 atms. Observed osmotic pressures:

	Atms.		Atms.
April 8, 10.00 A.M.	14.400	April 9, 10.00 A.M.	14.399
10.00 P.M.	14.378	2.00 P.M.	14.404
		Mean,	14.395
		Mean of experiments 1 and 2,	14.381
		Ratio of osmotic to gas pressure,	1.0765

Table LXXXII.

0.6 Wt. normal solution. Expt. 1 at 5°. Cell J_3. Resistance of membrane, 360,000 ohms. Manometer 11. Calc. gas pressure, 13.604 atms. Time of setting up cell, Feb. 1, 1909, 4.00 P.M. Initial pressure, 10.28 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 2, 9.00 A.M.	14.604	Feb. 3, 9.00 A.M.	14.602
1.00 P.M.	14.617	12.30 P.M.	14.591
		Mean,	14.604

Table LXXXIII.

0.6 Wt. normal solution. Expt. 2 at 5°. Cell L_3. Resistance of membrane, 370,000 ohms. Manometer 20. Calc. gas pressure, 13.604 atms. Time of setting up cell, Feb. 1, 1909, 4.00 P.M. Initial pressure, 13.59 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 2, 9.00 A.M.	14.611	Feb. 2, 4.30 P.M.	14.601
1.00 P.M.	14.604	3, 12.30 P.M.	14.608
		Mean,	14.606
		Mean of experiments 1 and 2,	14.605
		Ratio of osmotic to gas pressure,	1.074

Table LXXXIV.

0.6 Wt. normal solution. Expt. 1 at 10°. Cell H_3. Resistance of membrane, 78,000 ohms. Manometer 15. Calc. gas pressure, 13.849 atms. Time of setting up cell, April 6, 1909, 12.30 P.M. Initial pressure, 13.58 atms. Observed osmotic pressures:

	Atms.		Atms.
April 7, 9.00 A.M.	14.838	April 8, 10.00 A.M.	14.847
1.00 P.M.	14.878	2.00 P.M.	14.861
		Mean,	14.856

Table LXXXV.

0.6 Wt. normal solution. Expt. 2 at 10°. Cell J_3. Resistance of membrane, 112,000 ohms. Manometer 20. Calc. gas pressure, 13.849 atms. Time of setting up cell, April 6, 1909, 12.30 P.M. Initial pressure, 14.63 atms. Observed osmotic pressures:

	Atms.		Atms.
April 7, 9.00 A.M.	14.862	April 8, 10.00 A.M.	14.851
9.00 P.M.	14.847	2.00 P.M.	14.856
		Mean,	14.854
		Mean of experiments 1 and 2,	14.855
		Ratio of osmotic to gas pressure,	1.073

Table LXXXVI.

0.6 Wt. normal solution. Expt. 1 at 15°. Cell A_5. Resistance of membrane, 160,000 ohms. Manometer 9. Calc. gas pressure, 14.094 atms. Time of setting up cell, April 18, 1910, 12.00 M. Initial pressure, 14.7 atms. Observed osmotic pressures:

	Atms.		Atms.
April 18	15.148	April 23	15.130
19	15.149	24	15.128
20	15.126	25	15.123
21	15.125	26	15.117
22	15.115	27	15.116
		Mean,	15.128

Table LXXXVII.

0.6 Wt. normal solution. Expt. 2 at 15°. Cell A_5. Resistance of membrane, 140,000 ohms. Manometer 20. Calc. gas pressure, 14.094 atms. Time of setting up cell, Jan. 21, 1911, 12.00 M. Initial pressure, 14.568 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 24, 9.00 A.M.	15.185	Jan. 26, 9.00 A.M.	15.140
25, 9.00 A.M.	15.156	5.00 P.M.	15.157
5.00 P.M.	15.168	27, 9.00 A.M.	15.152
		Mean,	15.160
		Mean of experiments 1 and 2,	15.144
		Ratio of osmotic to gas pressure,	1.073

Table LXXXVIII.

0.6 Wt. normal solution. Expt. 1 at 20°. Cell Z_3. Resistance of membrane, 550,000 ohms. Manometer 6. Calc. gas pressure, 14.339 atms. Time of setting up cell, Nov. 12, 1909, 4.00 P.M. Initial pressure, 15.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 13, 5.00 P.M.	15.408	Nov. 15, 12.00 M.	15.381
11.00 P.M.	15.405	5.00 P.M.	15.427
		Mean,	15.405

Table LXXXIX.

0.6 Wt. normal solution. Expt. 2 at 20°. Cell O_3. Resistance of membrane, 350,000 ohms. Manometer 5. Calc. gas pressure, 14.339 atms. Time of setting up cell, Nov. 19, 1909, 12.00 M. Initial pressure, 14.10 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 20, 10.00 P.M.	15.365	Nov. 21, 11.00 P.M.	15.387
21, 12.00 M.	15.388	22, 10.00 A.M.	15.339
		Mean,	15.370
		Mean of experiments 1 and 2,	15.388
		Ratio of osmotic to gas pressure,	1.073

Table XC.

0.6 Wt. normal solution. Expt. 1 at 25°. Cell M_3. Resistance of membrane, 275,000 ohms. Manometer 11. Calc. gas pressure, 14.585 atms. Time of setting up cell, Nov. 22, 1909, 2.00 P.M. Initial pressure, 15.54 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 23, 5.00 P.M.	15.623	Nov. 25, 5.00 P.M.	15.628
24, 9.00 A.M.	15.619	26, 9.00 P.M.	15.659
		Mean,	15.632

Table XCI.

0.6 Wt. normal solution. Expt. 2 at 25°. Cell K_3. Resistance of membrane, 525,000 ohms. Manometer 9. Calc. gas pressure, 14.585 atms. Time of setting up cell, Nov. 24, 1909, 12.30 P.M. Initial pressure, 13.45 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 27	15.602	Nov. 29	15.624
28	15.627	30	15.606
		Mean,	15.615

Table XCII.

0.6 Wt. normal solution. Expt. 3 at 25°. Cell R_3. Resistance of membrane, 96,000 ohms. Manometer 9. Calc. gas pressure, 14.585 atms. Time of setting up cell, Nov. 10, 1910, 4.00 P.M. Initial pressure, 14.6 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 13	15.632	Nov. 15	15.619
14	15.619	16	15.609
		Mean,	15.620

Table XCIII.

0.6 Wt. normal solution. Expt. 4 at 25°. Cell Q_3. Resistance of membrane, 110,000 ohms. Manometer 15. Calc. gas pressure, 14.585 atms. Time of setting up cell, Nov. 10, 1910, 4.00 P.M. Initial pressure, 14.85 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 16	15.654	Nov. 20	15.628
19	15.623	21	15.629
		Mean,	15.634
		Mean of experiments 1, 2, 3 and 4,	15.625
		Ratio of osmotic to gas pressure,	1.071

Table XCIV.

0.7 Wt. normal solution. Expt. 1 at 0°. Cell M_2. Resistance of membrane, 515,000 ohms. Manometer 5. Calc. gas pressure, 15.586 atms. Time of setting up cell, Feb. 23, 1909, 2.00 P.M. Initial pressure, 16.82 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 24, 12.00 M.	16.897	Feb. 25, 12.30 P.M.	16.878
9.30 P.M.	16.878	5.00 P.M.	16.871
		Mean,	16.881

Table XCV.

0.7 Wt. normal solution. Expt. 2 at 0°. Cell D_3. Resistance of membrane, 280,000 ohms. Manometer 6. Calc. gas pressure, 15.586 atms. Time of setting up cell, Mar. 24, 1909, 2.30 P.M. Initial pressure, 16.59 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 25, 9.30 A.M.	16.897	Mar. 26, 11.00 P.M.	16.892
5.00 P.M.	16.907	27, 2.00 P.M.	16.867
		Mean,	16.891
		Mean of experiments 1 and 2,	16.886
		Ratio of osmotic to gas pressure,	1.083

Table XCVI.

0.7 Wt. normal solution. Expt. 1 at 5°. Cell M_3. Resistance of membrane, 275,000 ohms. Manometer 9. Calc. gas pressure, 15.872 atms. Time of setting up cell, Feb. 2, 1909, 2.30 P.M. Initial pressure, 15.51 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 3, 12.30 P.M.	17.235	Feb. 4, 9.30 A.M.	17.215
10.00 P.M.	17.220	3.00 P.M.	17.199
		Mean,	17.217

Table XCVII.

0.7 Wt. normal solution. Expt. 2 at 5°. Cell J_3. Resistance of membrane, 270,000 ohms. Manometer 6. Calc. gas pressure, 15.872 atms. Time of setting up cell, Feb. 11, 1909, 12.30 P.M. Initial pressure, 16.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 12, 1.00 P.M.	17.196	Feb. 13, 10.30 A.M.	17.192
5.00 P.M.	17.185	3.00 P.M.	17.204

Mean, 17.194

Mean of experiments 1 and 2, 17.206

Ratio of osmotic to gas pressure, 1.084

Table XCVIII.

0.7 Wt. normal solution. Expt. 1 at 10°. Cell F_3. Resistance of membrane, 278,000 ohms. Manometer 20. Calc. gas pressure, 16.157 atms. Time of setting up cell, Mar. 31, 1909, 12.30 P.M. Initial pressure, 16.73 atms. Observed osmotic pressures:

	Atms.		Atms.
April 1, 9.00 P.M.	17.478	April 2, 2.30 P.M.	17.498
2, 10.00 A.M.	17.486	10.00 P.M.	17.490

Mean, 17.488

Table XCIX.

0.7 Wt. normal solution. Expt. 2 at 10°. Cell P_3. Resistance of membrane, 191,000 ohms. Manometer 9. Calc. gas pressure, 16.157 atms. Time of setting up cell, April 14, 1909, 12.30 P.M. Initial pressure, 17.25 atms. Observed osmotic pressures:

	Atms.		Atms.
April 14, 5.30 P.M.	17.530	April 15, 5.30 P.M.	17.519
15, 2.00 P.M.	17.512	10.00 P.M.	17.511

Mean, 17.518

Mean of experiments 1 and 2, 17.503

Ratio of osmotic to gas pressure, 1.083

Table C.

0.7 Wt. normal solution. Expt. 1 at 15°. Cell Z_3. Resistance of membrane, 565,000 ohms. Manometer 9. Calc. gas pressure, 16.443 atms. Time of setting up cell, April 14, 1910, 12.30 P.M. Initial pressure, 16.5 atms. Observed osmotic pressures:

	Atms.		Atms.
April 16, 1.00 P.M.	17.820	April 17, 10.00 A.M.	17.820
8.00 P.M.	17.818	18, 10.00 A.M.	17.824

Mean, 17.821

Table CI.

0.7 Wt. normal solution. Expt. 2 at 15°. Cell M_3. Resistance of membrane, 220,000 ohms. Manometer 24. Calc. gas pressure, 16.443 atms. Time of setting up cell, Jan. 20, 1911, 12.30 P.M. Initial pressure, 17.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 21, 7.00 P.M.	17.811	Jan. 23, 4.00 P.M.	17.797
22, 6.00 P.M.	17.827	24, 9.00 A.M.	17.797
		Mean,	17.808
		Mean of experiments 1 and 2,	17.815
		Ratio of osmotic to gas pressure,	1.083

Table CII.

0.7 Wt. normal solution. Expt. 1 at 20°. Cell M_3. Resistance of membrane, 380,000 ohms. Manometer 6. Calc. gas pressure, 16.729 atms. Time of setting up cell, Dec. 2, 1909, 12.00 M. Initial pressure, 17.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 3, 5.00 P.M.	18.106	Dec. 4, 5.00 P.M.	18.142
4, 1.00 P.M.	18.183	5, 9.00 A.M.	18.110
		Mean,	18.135

Table CIII.

0.7 Wt. normal solution. Expt. 2 at 20°. Cell D_3. Resistance of membrane, 380,000 ohms. Manometer 5. Calc. gas pressure, 16.729 atms. Time of setting up cell, Dec. 2, 1909, 12.00 M. Initial pressure, 17.10 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 3, 5.00 P.M.	18.138	Dec. 4, 5.00 P.M.	18.085
4, 10.00 A.M.	18.115	5, 8.00 P.M.	18.146
		Mean,	18.121
		Mean of experiments 1 and 2,	18.128
		Ratio of osmotic to gas pressure,	1.084

Table CIV.

0.7 Wt. normal solution. Expt. 1 at 25°. Cell F_3. Resistance of membrane, 367,000 ohms. Manometer 9. Calc. gas pressure, 17.015 atms. Time of setting up cell, Dec. 17, 1909, 5.00 P.M. Initial pressure, 16.94 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 19	18.383	Dec. 21	18.445
20	18.471	22	18.445
		Mean,	18.436

Table CV.

0.7 Wt. normal solution. Expt. 2 at 25°. Cell M_3. Resistance of membrane, 560,000 ohms. Manometer 9. Calc. gas pressure, 17.015 atms. Time of setting up cell, Dec. 21, 1909, 12.00 M. Initial pressure, 18.84 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 21	18.419	Dec. 24	18.446
22	18.450	25	18.413
23	18.452	26	18.423
		Mean,	18.434
		Mean of experiments 1 and 2,	18.435
		Ratio of osmotic to gas pressure,	1.083

Table CVI.

0.8 Wt. normal solution. Expt. 1 at 0°. Cell H_3. Resistance of membrane, 366,000 ohms. Manometer 5. Calc. gas pressure, 17.812 atms. Time of setting up cell, Feb. 19, 1909, 4.00 P.M. Initial pressure, 19.10 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 20, 12.00 M.	19.487	Feb. 21, 11.00 A.M.	19.496
11.00 P.M.	19.482	22, 9.00 A.M.	19.478
		Mean,	19.486

Table CVII.

0.8 Wt. normal solution. Expt. 2 at 0°. Cell D_3. Resistance of membrane, 550,000 ohms. Manometer 11. Calc. gas pressure, 17.812 atms. Time of setting up cell, Feb. 19, 1909, 4.00 P.M. Initial pressure, 19.01 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 20, 11.00 P.M.	19.448	Feb. 21, 6.00 P.M.	19.470
21, 11.00 A.M.	19.495	22, 9.00 A.M.	19.452
		Mean,	19.466
		Mean of experiments 1 and 2,	19.476
		Ratio of osmotic to gas pressure,	1.093

Table CVIII.

0.8 Wt. normal solution. Expt. 1 at 5°. Cell J_3. Resistance of membrane, 275,000 ohms. Manometer 20. Calc. gas pressure, 18.139 atms. Time of setting up cell, Feb. 4, 1909, 12.30 P.M. Initial pressure, 19.50 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 4, 10.00 P.M.	19.797	Feb. 5, 9.30 P.M.	19.802
5, 1.00 P.M.	19.788	6, 12.00 M.	19.793
		Mean,	19.795

Table CIX.

0.8 Wt. normal solution. Expt. 2 at 5°. Cell B_3. Resistance of membrane, 550,000 ohms. Manometer 9. Calc. gas pressure, 18.139 atms. Time of setting up cell, Feb. 9, 1909, 3.00 P.M. Initial pressure, 16.61 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 10, 1.00 P.M.	19.844	Feb. 11, 9.00 A.M.	19.846
10.30 P.M.	19.853	2.30 P.M.	19.853
		Mean,	19.849
		Mean of experiments 1 and 2,	19.822
		Ratio of osmotic to gas pressure,	1.093

Table CX.

0.8 Wt. normal solution. Expt. 1 at 10°. Cell F_3. Resistance of membrane, 220,000 ohms. Manometer 20. Calc. gas pressure, 18.466 ohms. Time of setting up cell, Mar. 17, 1909, 12.30 P.M. Initial pressure, 17.60 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 18, 1.00 P.M.	20.156	Mar. 19, 9.00 A.M.	20.152
9.00 P.M.	20.167	4.30 P.M.	20.133
		Mean,	20.152

Table CXI.

0.8 Wt. normal solution. Expt. 2 at 10°. Cell L_3. Resistance of membrane, 234,000 ohms. Manometer 20. Calc. gas pressure, 18.466 atms. Time of setting up cell, Mar. 26, 1909, 3.00 P.M. Initial pressure, 18.72 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 27, 5.00 P.M.	20.159	Mar. 28, 5.00 P.M.	20.195
28, 12.00 M.	20.162	29, 9.00 A.M.	20.159
		Mean,	20.169
		Mean of experiments 1 and 2,	20.161
		Ratio of osmotic to gas pressure,	1.092

Table CXII.

0.8 Wt. normal solution. Expt. 1 at 15°. Cell Z_3. Resistance of membrane, 555,000 ohms. Manometer 9. Calc. gas pressure, 18.792 atms. Time of setting up cell, April 4, 1910, 4.00 P.M. Initial pressure, 19.5 atms. Observed osmotic pressures:

	Atms.		Atms.
April 5, 1.00 P.M.	20.500	April 6, 9.00 P.M.	20.531
6, 9.00 A.M.	20.547	7, 12.00 M.	20.554
		Mean,	20.533

Table CXIII.

0.8 Wt. normal solution. Expt. 2 at 15°. Cell H_5. Resistance of membrane, 110,000 ohms. Manometer 22. Calc. gas pressure, 18.792 atms. Time of setting up cell, Jan. 18, 1911, 2.00 P.M. Initial pressure, 19.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 21	20.505	Jan. 23	20.539
22	20.531		
		Mean,	20.525

Table CXIV.

0.8 Wt. normal solution. Expt. 3 at 15°. Cell E_5. Resistance of membrane, 150,000 ohms. Manometer 9. Calc. gas pressure, 18.792 atms. Time of setting up cell, Jan. 18, 1911, 2.00 P.M. Initial pressure, 19.6 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 20	20.550	Jan. 22	2 .539
21	20.545	23	20.557
		Mean,	20.548
		Mean of experiments 1, 2 and 3,	20.535
		Ratio of osmotic to gas pressure,	1.093

Table CXV.

0.8 Wt. normal solution. Expt. 1 at 20°. Cell Z_3. Resistance of membrane, 570,000 ohms. Manometer 5. Calc. gas pressure, 19.119 atms. Time of setting up cell, Nov. 26, 1909, 12.00 M. Initial pressure, 19.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 27, 10.00 A.M.	20.912	Nov. 27, 11.00 P.M.	20.931
1.00 P.M.	20.972	28, 11.00 P.M.	20.896
		Mean,	20.928

Table CXVI.

0.8 Wt. normal solution. Expt. 2 at 20°. Cell Z_2. Resistance of membrane, 275,000 ohms. Manometer 24. Calc. gas pressure, 19.119 atms. Time of setting up cell, Feb. 11, 1911, 1.00 P.M. Initial pressure, 19.3 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 12, 1.00 P.M.	20.900	Feb. 13, 11.00 P.M.	20.892
13, 6.00 P.M.	20.879	14, 1.00 P.M.	20.861
		Mean,	20.883

Table CXVII.

0.8 Wt. normal solution. Expt. 3 at 20°. Cell E_3. Resistance of membrane, 140,000 ohms. Manometer 9. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 8, 1910, 12.00 M. Initial pressure, 19.41 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 10	20.907	Dec. 13	20.922
11	20.857	14	20.922
12	20.866	15	20.918
		Mean,	20.899

Table CXVIII.

0.8 Wt. normal solution. Expt. 4 at 20°. Cell D_5. Resistance of membrane, 250,000 ohms. Manometer 6. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 8, 1910, 12.00 M. Initial pressure, 20.5 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 11	20.921	Dec. 14	20.912
12	20.907	15	20.915
13	20.891		
		Mean,	20.909
		Mean of experiments 1, 2, 3 and 4,	20.905
		Ratio of osmotic to gas pressure,	1.093

Table CXIX.

0.8 Wt. normal solution. Expt. 1 at 25°. Cell F_3. Resistance of membrane, 140,000 ohms. Manometer 9. Calc. gas pressure, 19.446 atms. Time of setting up cell, Jan. 4, 1910, 3.00 P.M. Initial pressure, 19.06 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 5	21.281	Jan. 12	21.238
6	21.253	13	21.266
7	21.256	14	21.257
8	21.281	15	21.249
9	21.280	16	21.249
10	21.258	17	21.246
11	21.238	18	21.264
		Mean,	21.258

Table CXX.

0.8 Wt. normal solution. Expt. 2 at 25°. Cell W_3. Resistance of membrane, 367,000 ohms. Manometer 11. Calc. gas pressure, 19.446 atms. Time of setting up cell, Jan. 6, 1910, 2.00 P.M. Initial pressure, 20.77 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 8, 12.00 M.	21.252	Jan. 10, 11.00 P.M.	21.257
10, 1.00 P.M.	21.225	11, 11.00 A.M.	21.267
		Mean,	21.250

Mean of experiments 1 and 2, 21.254
Ratio of osmotic to gas pressure, 1.093

Table CXXI.

0.9 Wt. normal solution. Expt. 1 at 0°. Cell F_3. Resistance of membrane, 550,000 ohms. Manometer 11. Calc. gas pressure, 20.04 atms. Time of setting up cell, Feb. 17, 1909, 3.00 P.M. Initial pressure, 21.45 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 18, 8.30 A.M.	22.163	Feb. 19, 9.00 A.M.	22.130
5.00 P.M.	22.162	12.00 M.	22.140
		Mean,	22.149

Table CXXII.

0.9 Wt. normal solution. Expt. 2 at 0°. Cell D_3. Resistance of membrane, 160,000 ohms. Manometer 5. Calc. gas pressure, 20.04 atms. Time of setting up cell, Mar. 11, 1909, 2.30 P.M. Initial pressure, 21.78 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 12, 10.00 A.M.	22.075	Mar. 12, 10.00 P.M.	22.106
12.00 M.	22.079	13, 12.00 M.	22.086
		Mean,	22.087

Mean of experiments 1 and 2, 22.118
Ratio of osmotic to gas pressure, 1.104

Table CXXIII.

0.9 Wt. normal solution. Expt. 1 at 5°. Cell B_3. Resistance of membrane, 500,000 ohms. Manometer 9. Calc. gas pressure, 20.406 atms. Time of setting up cell, Jan. 18, 1909, 3.00 P.M. Initial pressure, 17.11 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 20, 10.00 A.M.	22.46	Jan. 22, 5.00 A.M.	22.53
21, 1.00 A.M.	22.53	9.00 A.M.	22.53
		Mean,	22.513

Table CXXIV.

0.9 Wt. normal solution. Expt. 2 at 5°. Cell Q_3. Resistance of membrane, 550,000 ohms. Manometer 20. Calc. gas pressure, 20.406 atms. Time of setting up cell, Feb. 19, 1909, 3.00 P.M. Initial pressure, 22.06 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 22, 9.00 A.M.	22.448	Feb. 22, 10.00 P.M.	22.445
3.00 P.M.	22.447	23, 9.00 A.M.	22.433
		Mean,	22.443
		Mean of experiments 1 and 2,	22.478
		Ratio of osmotic to gas pressure,	1.102

Table CXXV.

0.9 Wt. normal solution. Expt. 1 at 10°. Cell F_3. Resistance of membrane, 220,000 ohms. Manometer 9. Calc. gas pressure, 20.774 atms. Time of setting up cell, Mar. 24, 1909, 12.30 P.M. Initial pressure, 19.45 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 25, 5.00 P.M.	22.915	Mar. 26, 9.00 A.M.	22.915
9.00 P.M.	22.912	5.00 P.M.	22.902
		Mean,	22.911

Table CXXVI.

0.9 Wt. normal solution. Expt. 2 at 10°. Cell B_3. Resistance of membrane, 138,000 ohms. Manometer 21. Calc. gas pressure, 20.774 atms. Time of setting up cell, April 13, 1909, 12.30 P.M. Initial pressure, 19.02 atms. Observed osmotic pressures:

	Atms.		Atms.
April 14, 10.00 P.M.	22.860	April 15, 2.00 P.M.	22.857
15, 10.00 A.M.	22.866	9.00 P.M.	22.846
		Mean,	22.857
		Mean of experiments 1 and 2,	22.884
		Ratio of osmotic to gas pressure,	1.102

Table CXXVII.

0.9 Wt. normal solution. Expt. 1 at 15°. Cell T_3. Resistance of membrane, 185,000 ohms. Manometer 9. Calc. gas pressure, 21.141 atms. Time of setting up cell, April 28, 1910, 12.00 M. Initial pressure, 20.5 atms. Observed osmotic pressures:

	Atms.		Atms.
April 29, 9.00 A.M.	23.325	April 30, 5.00 P.M.	23.311
30, 9.00 A.M.	23.321	May 1, 11.00 A.M.	23.300
		Mean,	23.314

Table CXXVIII.

0.9 Wt. normal solution. Expt. 2 at 15°. Cell R_3. Resistance of membrane, 330,000 ohms. Manometer 20. Calc. gas pressure, 21.141 atms. Time of setting up cell, Jan. 16, 1911, 3.00 P.M. Initial pressure, 22.711 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 19, 11.00 A.M.	23.338	Jan. 20, 12.00 M.	23.282
5.00 P.M.	23.309	5.00 P.M.	23.254
		Mean,	23.296
		Mean of experiments 1 and 2,	23.305
		Ratio of osmotic to gas pressure,	1.102

Table CXXIX.

0.9 Wt. normal solution. Expt. 1 at 20°. Cell D_3. Resistance of membrane, 550,000 ohms. Manometer 15. Calc. gas pressure, 21.509 atms. Time of setting up cell, Mar. 17, 1909, 12.00 M. Initial pressure, 20.40 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 18	23.721	Mar. 20	23.727
19	23.707	21	23.701
		Mean,	23.715

Table CXXX.

0.9 Wt. normal solution. Expt. 2 at 20°. Cell A_5. Resistance of membrane, 250,000 ohms. Manometer 22. Calc. gas pressure, 21.509 atms. Time of setting up cell, Dec. 6, 1910, 12.00 M. Initial pressure, 20.65 atms. Observed osmotic pressures:

	Atms.		Atms.
Dec. 7	23.703	Dec. 10	23.733
8	23.702	11	23.731
9	23.702	12	23.734
		Mean,	23.718
		Mean of experiments 1 and 2,	23.717
		Ratio of osmotic to gas pressure,	1.103

Table CXXXI.

0.9 Wt. normal solution. Expt. 1 at 25°. Cell D_3. Resistance of membrane, 220,000 ohms. Manometer 9. Calc. gas pressure, 21.877 atms. Time of setting up cell, Jan. 20, 1910, 4.00 P.M. Initial pressure, 20.28 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 21	24.127	Jan. 24	24.102
22	24.148	25	24.125
23	24.120		
		Mean,	24.126

Table CXXXII.

0.9 Wt. normal solution. Expt. 2 at 25°. Cell B_5. Resistance of membrane, 550,000 ohms. Manometer 9. Calc. gas pressure, 21.877 atms. Time of setting up cell, Oct. 29, 1910, 12.00 M. Initial pressure, 22.2 atms. Observed osmotic pressures:

	Atms.		Atms.
Oct. 30, 11.00 A.M.	24.126	Nov. 1, 5.00 P.M.	24.133
31, 9.00 A.M.	24.114	2, 9.00 A.M.	24.124
Nov. 1, 9.00 A.M.	24.128		

Mean, 24.125
Mean of experiments 1 and 2, 24.126
Ratio of osmotic to gas pressure, 1.102

Table CXXXIII.

1.0 Wt. normal solution. Expt. 1 at 0°. Cell D_3. Resistance of membrane, 180,000 ohms. Manometer 20. Calc. gas pressure, 22.265 atms. Time of setting up cell, Jan. 20, 1909, 4.00 P.M. Initial pressure, 24.35 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 21, 9.00 P.M.	24.883	Jan. 22, 5.00 P.M.	24.891
22, 12.00 M.	24.864	23, 9.00 A.M.	24.864

Mean, 24.878

Table CXXXIV.

1.0 Wt. normal solution. Expt. 2 at 0°. Cell D_3. Resistance of membrane, 555,000 ohms. Manometer 11. Calc. gas pressure, 22.265 atms. Time of setting up cell, Feb. 13, 1909, 3.00 P.M. Initial pressure, 24.63 atms. Observed osmotic pressures:

	Atms.		Atms.
Feb. 14, 11.00 P.M.	24.760	Feb. 15, 1.00 P.M.	24.798
5.00 P.M.	24.763	16, 9.00 A.M.	24.776

Mean, 24.774
Mean of experiments 1 and 2, 24.825
Ratio of osmotic to gas pressure, 1.115

Table CXXXV.

1.0 Wt. normal solution. Expt. 1 at 5°. Cell F_3. Resistance of membrane, 1,000,000 ohms. Manometer 21. Calc. gas pressure, 22.67 atms. Time of setting up cell, Jan. 13, 1909, 4.30 P.M. Initial pressure 18.56 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 14, 1.00 P.M.	25.31	Jan. 15, 9.00 A.M.	25.27
15, 12.30 A.M.	25.32	16, 12.30 P.M.	25.29

Mean, 25.298

Table CXXXVI.

1.0 Wt. normal solution. Expt. 2 at 5°. Cell S. Resistance of membrane, 550,000 ohms. Manometer 20. Calc. gas pressure, 22.67 atms. Time of setting up cell, Jan. 16, 1909, 12.00 M. Initial pressure, 20.12 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 18, 5.00 A.M.	25.30	Jan. 19, 9.00 A.M.	25.32
9.30 P.M.	25.28	1.00 P.M.	25.30
		Mean,	25.30

Table CXXXVII.

1.0 Wt. normal solution. Expt. 3 at 5°. Cell K_3. Resistance of membrane, 1,100,000 ohms. Manometer 9. Calc. gas pressure, 22.67 atms. Time of setting up cell, Jan. 16, 1909, 12.30 P.M. Initial pressure, 21.83 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 16, 9.00 P.M.	25.32	Jan. 17, 11.00 A.M.	25.31
17, 7.30 A.M.	25.31	9.00 P.M.	25.26
		Mean,	25.30

Table CXXXVIII.

1.0 Wt. normal solution. Expt. 4 at 5°. Cell J_3. Resistance of membrane, 1,100,000 ohms. Manometer 21. Calc. gas pressure, 22.67 atms. Time of setting up cell, Jan. 16, 1909, 12.30 P.M. Initial pressure, 20.15 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 16, 9.00 P.M.	25.23	Jan. 18, 5.00 A.M.	25.25
17, 9.00 A.M.	25.25	10.00 P.M.	25.23
		Mean,	25.24

Table CXXXIX.

1.0 Wt. normal solution. Expt. 5 at 5°. Cell G_3. Resistance of membrane, 550,000 ohms. Manometer 22. Calc. gas pressure, 22.67 atms. Time of setting up cell, Jan. 19, 1909, 4.00 P.M. Initial pressure, 20.91 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 20, 10.00 A.M.	25.26	Jan. 21, 9.00 A.M.	25.24
21, 5.00 A.M.	25.25	1.00 P.M.	25.28
		Mean,	25.258

Mean of experiments 1, 2, 3, 4 and 5, 25.283
Ratio of osmotic to gas pressure, 1.115

Table CXL.

1.0 Wt. normal solution. Expt. 1 at 10°. Cell F_3. Resistance of membrane, 550,000 ohms. Manometer 6. Calc. gas pressure, 20.082 atms. Time of setting up cell, Mar. 3, 1909, 12.30 P.M. Initial pressure, 23.83 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 5, 9.30 A.M.	25.682	Mar. 6, 9.30 A.M.	25.692
1.00 P.M.	25.746	1.00 P.M.	25.695
		Mean,	25.704

Table CXLI.

1.0 Wt. normal solution. Expt. 2 at 10°. Cell B_3. Resistance of membrane, 220,000 ohms. Manometer 20. Calc. gas pressure, 23.082 atms. Time of setting up cell, Mar. 3, 1909, 12.30 P.M. Initial pressure, 22.46 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 5, 9.30 A.M.	25.704	Mar. 5, 10.00 P.M.	25.684
5.00 P.M.	25.671	6, 1.00 P.M.	25.670
		Mean,	25.682

Mean of experiments 1 and 2, 25.693
Ratio of osmotic to gas pressure, 1.113

Table CXLII.

1.0 Wt. normal solution. Exps. 1 at 15°. Cell G_3. Resistance of membrane, 370,000 ohms. Manometer 9. Calc. gas pressure, 23.49 atms. Time of setting up cell, April 11, 1910, 1.00 P.M. Initial pressure, 26.05 atms. Observed osmotic pressures:

	Atms.		Atms.
April 12, 12.00 M.	26.212	April 13, 4.00 P.M.	26.194
9.00 P.M.	26.211	14, 12.00 M.	26.207
		Mean,	26.206

Table CXLIII.

1.0 Wt. normal solution. Expt. 2 at 15°. Cell D_3. Resistance of membrane, 355,000 ohms. Manometer 15. Calc. gas pressure, 23.49 atms. Time of setting up cell, April 11, 1910, 1.00 P.M. Initial pressure, 26.00 atms. Observed osmotic pressures:

	Atms.		Atms.
April 13, 4.00 P.M.	26.182	April 15, 9.00 A.M.	26.131
14, 9.00 A.M.	26.180	3.00 P.M.	26.192
		Mean,	26.171

Mean of experiments 1 and 2, 26.189
Ratio of osmotic to gas pressure, 1.115

Table CXLIV.

1.0 Wt. normal solution. Expt. 1 at 20°. Cell P. Resistance of membrane, 370,000 ohms. Manometer 21. Calc. gas pressure, 23.899 atms. Time of setting up cell, Mar. 3, 1910, 4.00 P.M. Initial pressure, 23.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Mar. 4	26.629	Mar. 6	26.663
5	26.654	7	26.645
		Mean,	26.648

Table CXLV.

1.0 Wt. normal solution. Expt. 2 at 20°. Cell H_5. Resistance of membrane, 200,000 ohms. Manometer 22. Calc. gas pressure, 23.899 atms. Time of setting up cell, Nov. 29, 1910, 4.00 P.M. Initial pressure, 25.19 atms. Observed osmotic pressures:

	Atms.		Atms.
Nov. 30	26.620	Dec. 2	26.644
Dec. 1	26.645	3	26.598
		Mean,	26.627
		Mean of experiments 1 and 2,	26.638
		Ratio of osmotic to gas pressure,	1.115

Table CXLVI.

1.0 Wt. normal solution. Expt. 1 at 25°. Cell E_3. Resistance of membrane, 550,000 ohms. Manometer 15. Calc. gas pressure, 24.308 atms. Time of setting up cell, Jan. 26, 1910, 12.00 M. Initial pressure, 26.95 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 27	27.113	Jan. 30	26.971
28	27.081	31	26.976
29	27.000		
		Mean,	27.030

Table CXLVII.

1.0 Wt. normal solution. Expt. 2 at 25°. Cell W_3. Resistance of membrane, 366,000 ohms. Manometer 9. Calc. gas pressure, 24.308 atms. Time of setting up cell, Jan. 26, 1910, 12.00 M. Initial pressure, 26.00 atms. Observed osmotic pressures:

	Atms.		Atms.
Jan. 28	27.024	Jan. 30	27.101
29	27.106	31	27.074
		Mean,	27.0763
		Mean of experiments 1 and 2,	27.053
		Ratio of osmotic to gas pressure,	1.113

Table CXLVIII.

	Wt. normal conc. 0.1.			0.2.			0.3.			0.4.			0.5.		
	O.P.	M.O.P.	Ratio.	O. P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.
0°				4.719											
0°	2.460			4.717			7.078								
0°	2.464			4.730			7.107			9.450			11.907		
0°	2.463	2.462	(1.106)	4.726	4.722	1.061	7.071	7.085	1.061	9.435	9.442	1.060	11.882	11.895	1.068
5°	2.452									9.623					
5°	2.451			4.812			7.187			9.584			12.100		
5°	2.453	2.452	1.082	4.825	4.818	1.063	7.209	7.198	1.058	9.617	9.608	1.059	12.100	12.100	1.067
10°	2.494														
10°	2.496														
10°	2.502			4.890			7.332			9.791			12.296		
10°	2.498	2.498	1.082	4.896	4.893	1.060	7.337	7.334	1.059	9.790	9.790	1.060	12.298	12.297	1.066
15°	2.547														
15°	2.535														
15°	2.541			4.981			7.465			9.950			12.565		
15°	2.538	2.541	1.082	4.988	4.985	1.061	7.486	7.476	1.061	9.947	9.948	1.059	12.533	12.549	1.068
20°				5.058											
20°				5.056											
20°				5.066			7.586								
20°	2.589			5.065			7.624			10.136			12.742		
20°	2.590	2.590	1.084	5.074	5.064	1.062	7.606	7.605	1.060	10.138	10.137	1.060	12.754	12.748	1.067
25°							7.735						12.932		
25°				5.154			7.719						12.972		
25°	2.635			5.139			7.722			10.298			12.919		
25°	2.632	2.634	1.084	5.150	5.148	1.059	7.738	7.729	1.060	10.295	10.296	1.059	12.947	12.943	1.065

Table CXLVIII (continued).

	Wt. normal conc. 0.6.			0.7.			0.8.			0.9.			1.0.		
	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.	O.P.	M.O.P.	Ratio.
0°	14.367			16.881			19.486			22.149			24.876		
0°	14.395	14.381	1.076	16.891	16.886	1.083	19.466	19.476	1.093	22.087	22.118	1.104	24.774	24.825	1.115
5°													25.298		
5°													25.300		
5°													25.300		
5°	14.604			17.217			19.795			22.443			25.240		
5°	14.606	14.605	1.074	17.194	17.206	1.084	19.849	19.822	1.093	22.513	22.478	1.102	25.258	25.283	1.115
10°	14.856			17.488			20.152			22.911			25.704		
10°	14.854	14.855	1.073	17.518	17.503	1.083	20.169	20.161	1.092	22.857	22.884	1.102	25.682	25.693	1.113
15°							20.533								
15°	15.128			17.821			20.525			23.314			26.206		
15°	15.160	15.144	1.073	17.808	17.815	1.083	20.548	20.535	1.093	23.296	23.305	1.102	26.171	26.189	1.115
20°							20.928								
20°							20.883								
20°	15.405			18.135			20.899			23.715			26.648		
20°	15.370	15.388	1.073	18.121	18.128	1.084	20.909	20.905	1.093	23.718	23.717	1.103	26.627	26.638	1.115
25°	15.632														
25°	15.615														
25°	15.620			18.436			21.250			24.126			27.030		
25°	15.634	15.625	1.071	18.434	18.435	1.083	21.258	21.254	1.093	24.125	24.126	1.102	27.076	27.053	1.113

Table CXLIX.

	Weight-normal concentration.									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Mean osmotic pressure in atmospheres.									
Temp.										
0°	(2.462)	4.722	7.085	9.442	11.895	14.381	16.886	19.476	22.118	24.825
5°	2.452	4.818	7.198	9.608	12.100	14.605	17.206	19.822	22.478	25.283
10°	2.498	4.893	7.334	9.790	12.297	14.855	17.503	20.161	22.884	25.693
15°	2.541	4.985	7.476	9.949	12.549	15.144	17.815	20.535	23.305	26.189
20°	2.590	5.064	7.605	10.137	12.748	15.388	18.128	20.905	23.717	26.638
25°	2.634	5.148	7.729	10.296	12.943	15.624	18.434	21.254	24.126	27.053

Table CL.

	Weight-normal concentration.									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of osmotic to gas pressure.									
Temp.										
0°	(1.106)	1.061	1.061	1.060	1.0685	1.0765	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
Mean.	1.083	1.061	1.060	1.060	0.067	1.074	1.083	1.093	1.103	1.114

The test of the law of Gay-Lussac as applied to osmotic pressure, within the range covered by this investigation, is the *constancy of the ratios* of osmotic to gas pressure in the several vertical columns of Table CL. It will be noted that this ratio *is constant*, within the necessary experimental errors, for each concentration, except in the case of the 0.1 weight-normal solution at 0°, which appears to constitute an exception to the rule otherwise applicable throughout. The ratio of osmotic to gas pressure in the 0.1 weight-normal solution at 0° is 1.106, instead of 1.082 to 1.084, as it was found to be at 5°, 10°, 15°, 20° and 25°, and the osmotic pressure is higher at 0° than at 5°. It is to be remembered in this connection as possibly explaining the anomaly that at 0° the 0.1 normal solution is within less than 0°.2 of its freezing temperature. It will be necessary, however, to ascertain whether the more concentrated solutions exhibit the same peculiarity at temperatures very near their freezing points before any satisfactory discussion of the matter can be undertaken. It will be observed, on referring to Table

CXLVIII, that more than the usual number of determinations of osmotic pressure were made with the 0.1 normal solution at 0°, 5,° 10° and 15,° and also with the 0.2 normal solution at 0°. This was done with a view to ascertaining with greater certainty whether the anomaly in question really exists. In order that the 0.1 normal solution should conform at 0° with what was found to be true in the case of all the other concentrations, its osmotic pressure must be about $2.227 \times 1.083 = 2.413$ atmospheres, instead of 2.462 atmospheres. The difference, 0.049 atmosphere, can hardly be ascribed to experimental errors in the case of a solution so dilute that unavoidable errors of meniscus and capillary depression are of little weight. Neither can it be ascribed to *thermometer effects*, since these were absent in the work at 0°.

If we except the 0.1 weight-normal solution at 0°, there is no longer any doubt in our minds that the osmotic pressures of all solutions containing from 0.1 to 1.0 gram-molecular weight of cane sugar in 1000 grams of water obey the law of Gay-Lussac between 0° and 25°. Nevertheless, we shall show in our next paper that the ratios of osmotic to gas pressure, which are so constant for each concentration between 0° and 25°, begin to decline at some temperature between 25° and 30°, and that the rate of decrease at higher temperatures is such as to lead one to suspect that the ratios will become unity for all concentrations at temperatures below the boiling point of the solvent. Such conduct on the part of cane sugar solutions can, of course, be ascribed with great plausibility to hydrates which are stable between 0° and 25°, but which gradually dissociate at higher temperatures However, discussion along this, or any other similar line, appears to us unprofitable until much more has been learned about the osmotic pressures of aqueous solutions of other substances than cane sugar.

JOHNS HOPKINS UNIVERSITY,
March 31, 1911.

ON THE ADDITION OF HYDROCYANIC ACID TO UNSATURATED COMPOUNDS.

[PRELIMINARY NOTE.]

BY PHILIP H. COBB.

In the course of an investigation of phenylmaleic and -fumaric acids which is in progress in this laboratory, it was discovered that when phenylpropiolic ester is treated with potassium cyanide by the method of Bredt and Kallen,[1] potassium carbonate and the nitrile of phenylsuccinic acid result. The mixture of the ester, dissolved in alcohol, and of an aqueous solution of two equivalents of potassium cyanide is boiled for some hours on the water bath. After filtering off the potassium carbonate the nitrile is obtained by the evaporation of the alcohol. It melts at 68°–69° when crystallized from water or diluted alcohol. It dissolves readily in cold chloroform, acetone, and strong alcohol, difficultly in cold, readily in hot carbon tetrachloride; it is practically insoluble in cold water, readily in hot. When warmed on the water bath with concentrated aqueous potassium hydroxide, ammonia is evolved. After the evolution has ceased the liquid is filtered from a little impurity and acidified. The precipitate crystallized from water melts at 165°–166° and is identical with phenylsuccinic acid prepared by another method. The melting point of a mixture of the two is the same.

A determination of the nitrogen in the compound gave the following values:

0.2020 gram substance gave 31 cc. nitrogen (absolute) measured over water; barometer, 772 mm.; thermometer, 19°.

	Calculated for $C_{10}H_8N_2$.	Found.
N	17.91	17.92

The reaction takes place as follows:

$$C_6H_5C:C.COOC_2H_5 + 2KCN + 2H_2O = C_6H_5.CHCN.CH_2.CN + K_2CO_3 + C_2H_5OH.$$

It is proposed to extend this research at once to other un-

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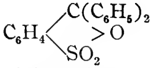
[1] Ann. Chem. (Liebig), **294**, 338.

saturated acids and to certain unsaturated hydrocarbons as well.

Tufts College, Mass.,
Apr. 10, 1911.

A FURTHER INVESTIGATION OF CERTAIN DERIVATIVES OF *o*-SULPHOBENZOIC ACID.

By Philip H. Cobb and George P. Fuller.

Remsen and Saunders[1] obtained the lactone  $C_6H_4\left\langle\begin{matrix}C(C_6H_5)_2\\ >O\\ SO_2\end{matrix}\right.$ once, through the action of benzene and aluminium chloride on a mixture of the chlorides of *o*-sulphobenzoic acid. They were unable to obtain these results again. Fritzsch[2] and List and Stein[3] also made it by the same method. One of us[4] repeated the above experiment but failed to get the lactone. It was obtained,[5] however, by the action of phenylmagnesium bromide on the anhydride of *o*-sulphobenzoic acid.[6] The substance thus prepared melted at 162°–163°, and agreed in its chemical properties with that obtained by the above investigators.

In his article on the action of organo-metallic compounds on alkylated saccharins, F. Sachs[7] subjected several products thus prepared to the action of fuming hydrochloric acid in sealed tubes, and also to the action of concentrated sulphuric acid. In the case of the products containing only alkyl groups in the side chains, the treatment yielded sultams with sul-

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[1] This Journal, **17**, 347.

[2] Ber. d. chem. Ges., **29**, 2288.

[3] *Ibid.*, **31**, 1664.

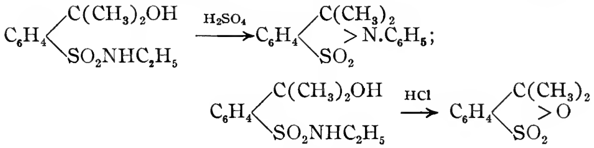
[4] Cobb: This Journal, **35**, 498.

[5] *Ibid.*, p. 507.

[6] This substance was also prepared by the action of phenylmagnesium bromide on the low-melting chloride of *o*-sulphobenzoic acid. Analysis: 0.1984 gram substance gave 0.0802 gram H_2O and 0.5098 gram CO_2. Calculated for $C_{19}H_{14}O_3S$: H 4.34, C 70.76; found: H 4.53, C 70.08. The identity of the two substances was also established by taking a melting point of the mixture. It remained 163°. This reaction is analogous to the action of zinc ethyl on succinyl chloride, which gives γ-diethylhydroxybutyrolactone. Neither of these reactions can be considered as conclusive evidence for the structure of the corresponding chloride, as it is impossible to say that both of the chlorine atoms are substituted by direct replacement. The high-melting chloride of *o*-sulphobenzoic acid gives triphenylcarbinol-*o*-phenylsulphone with phenylmagnesium bromide (see This Journal, **35**, 504).

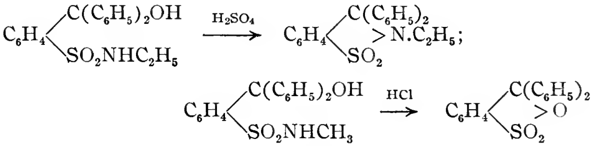
[7] Ber. d. chem. Ges., **37**, 3252.

phuric acid, and sultones with hydrochloric acid, as follows:

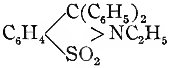


These products were well identified and undoubtedly possess the structure assigned to them.

Sachs also tried the action of hydrochloric and sulphuric acids on *N*-alkyl triphenylcarbinol-*o*-sulphonamides, with results represented as follows:



The conduct of these substances is apparently the same as that of the corresponding substances mentioned above, having alkyl groups in the place of phenyl. The analytical results for the sultam



are given, but not those for the substance obtained by the action of hydrochloric acid. Its melting point is 210°. The structure assigned to it, as well as its composition, is apparently based upon analogy to that of the compounds obtained in the corresponding reaction of those substances containing alkyl groups in the place of phenyl. Sachs remarks that the lactone obtained by Fritzsch (melting at 163°) was probably not pure.

If the substance obtained by Sachs were really the lactone, it follows that the compound previously described as the lactone was another substance, or else, as Sachs suggests, not entirely pure. The considerable difference in the melting point, however, did not seem to warrant this assumption. To settle the point the work of Sachs, as far as it relates to this substance, was repeated.

Following his directions,[1] 20 grams of methylsaccharin were treated with 52 grams of phenylmagnesium bromide. The reaction product was crystallized from absolute alcohol and melted at 194°, thus agreeing with the melting point of the Sachs compound.

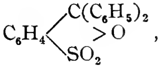
Three grams of this substance were heated with 80 cc. of fuming hydrochloric acid in a sealed tube for 15 hours at 150°. The reaction mixture was neutralized with sodium carbonate, filtered, and the solid remaining crystallized repeatedly from absolute alcohol. The melting point was 211°–212° (uncorr.), somewhat higher than that given by Sachs (210°). The presence of nitrogen was suspected, tested for, and proved.

Analysis:

0.3799 gram substance gave 0.016756 gram nitrogen (absolute).

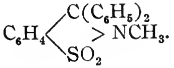
	Calculated for $C_{20}H_{17}O_2NS$.	Found.
N	4.18	4.41

It appears that the Sachs compound, to which he gave the formula of the sultone,



$$C_6H_4\begin{cases} C(C_6H_5)_2 \\ \qquad > O \\ SO_2 \end{cases},$$

is not this substance, but instead is the nitrogen compound, the sultam,



$$C_6H_4\begin{cases} C(C_6H_5)_2 \\ \qquad > NCH_3. \\ SO_2 \end{cases}$$

To test the action of sulphuric acid on triphenylcarbinol-*o*-sulphonic methylamide, 2 grams of that substance were allowed to stand with concentrated sulphuric acid for 12 hours at about 50°. The mixture was colored deep red. It was poured on ice, and the resulting white solid was crystallized from absolute alcohol. It melted at 210°–211°. Mixtures

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[1] *Loc. cit.*, p. 3267.

of the sulphuric and hydrochloric acid products melted at the same temperature. Furthermore, on analysis the substance gave the following results:

0.3792 gram substance gave 0.017147 gram nitrogen (absolute).

	Calculated for $C_{20}H_{17}O_2NS$.	Found.
N	4.18	4.52

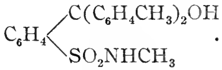
Thus the identity of the substances formed by the two methods is proved. It seemed interesting to determine whether this action of hydrochloric acid on compounds of this type is general. Accordingly, phenylditolylcarbinol - *o* - sulphonic methylamide was prepared by the action of tolylmagnesium bromide (from *p*-bromtoluene) on methylsaccharin. The reaction product was boiled with alcohol to free it from an oily by-product, and was then crystallized from acetone. It melted at 243° (uncorr.). The compound is insoluble in ether and ligroin; slightly soluble in absolute alcohol, acetone, chloroform, benzene, toluene, and xylene.

Analysis:

0.3007 gram substance gave 0.0105546 gram nitrogen (absolute).

	Calculated for $C_{22}H_{23}O_3NS$.	Found.
N	3.68	3.51

From the method of its formation and the results of the analysis it is probable that the compound has the formula



$$C_6H_4\begin{cases} C(C_6H_4CH_3)_2OH \\ SO_2NHCH_3 \end{cases}.$$

The action of fuming hydrochloric acid was tried. The substance was heated with this reagent for 14 hours at 150°. The reaction mixture was then neutralized, filtered, and the product crystallized from alcohol. It melted at 243°. The reaction was also tried at 200° but no change took place. The action of concentrated sulphuric acid was tried as in the previous experiment, once at room temperature for 12 hours, again at 40° for 12 hours, and finally at 70° for the same length of time. No change took place, however. The melting point after the treatment remained unchanged.

SUMMARY.

By identifying the Sachs compound as the sultam all doubt as to the identity of the lactone obtained by one of us[1] has been removed.

Sachs has shown that in at least two cases the action of hydrochloric and sulphuric acids is different. This difference exists where the compounds treated were obtained from alkyl saccharins by the action of alkyl magnesium halides. In their action on these compounds obtained from phenylmagnesium bromide and methylsaccharin, however, sulphuric and hydrochloric acids give the same product.

The attempt to obtain a reaction between hydrochloric or sulphuric acids and the ditolyl compound showed that this substance is too stable to be attacked by these reagents.

With sulphuric acid the reaction always takes place, if at all, with the elimination of water and the formation of the sultam. This is the normal action of this reagent, and it would remove water from compounds of this type if its affinity for water, aided by the conditions of the experiment, could overcome the resistance to its removal. It is seen above that the limit is reached in the ditolyl compound. For concentrated sulphuric acid to remove the elements of an amine would be impossible, as the first step in this process must be a hydrolysis, and the tendency to hydrolysis could never become great enough to take water out of concentrated sulphuric acid.

With concentrated hydrochloric acid, if the radicals of the side chain CR_2OH are aliphatic, the elements of an amine are removed and a sultone is formed. If they are phenyl groups, however, water is removed and a sultam is formed.

Concentrated hydrochloric acid is a substance which acts as a hydrolyzing agent in many cases, and which also possesses an affinity for water. Which of these properties it displays in a given case will depend upon the nature of the substance attacked, and the reaction taking place will be the

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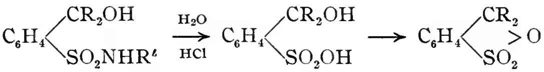
[1] Cobb: *Loc. cit.*

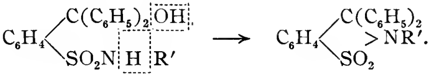
one which leaves the system in the better state of chemical neutralization. In the case of compounds of the type  $C_6H_4\left\langle\begin{array}{l}CR_2OH\\SO_2NHR'\end{array}\right.$, which differ among themselves only that in one case R represents an aliphatic radical and in the other phenyl, it is evident that the different action of hydrochloric acid is due to the different effect of the two kinds of radicals in this class of substances.

When the radicals are aliphatic the formation of the sultone is due to hydrolysis and the subsequent splitting out of water, thus:



$$C_6H_4\left\langle\begin{array}{l}CR_2OH\\SO_2NHR'\end{array}\right. \xrightarrow[HCl]{H_2O} C_6H_4\left\langle\begin{array}{l}CR_2OH\\SO_2OH\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{l}CR_2\\ \quad >O\\SO_2\end{array}\right.$$

and where the radicals are phenyl a simple dehydration takes place, thus:



$$C_6H_4\left\langle\begin{array}{l}C(C_6H_5)_2\,OH\\SO_2N\,H\,R'\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{l}C(C_6H_5)_2\\ \quad >NR'.\\SO_2\end{array}\right.$$

The causes bringing about the first series of reactions are the affinity of hydrochloric acid for the amine and the increase in chemical neutralization due to the splitting out of water from the hydrolyzed product. The opposing force is due to the resistance of the original compound to hydrolysis. The sum of these opposite forces is positive and the result is a number of reactions whose effect is exothermic. Therefore, under the conditions of the experiment (high temperature and pressure), the progress of these reactions results in a better state of chemical neutralization. At ordinary temperatures the resistance to hydrolysis is so great that the reaction does not take place.

In the second case, where the radicals are phenyl groups, the reaction proceeds quite differently. In this case the loss of water has become a chemical act opposed by less resistance than was the case in the preceding class of compounds, and which is also more easily effected than the loss of an amine by hydrolysis. This is probably due to the effect of the phenyl groups in facilitating dehydration, as is the case in the following acids: Phthalic acid loses water more easily than succinic, phenylsuccinic more easily than methylsuccinic, and phenylmaleic more easily than citraconic.

While the union of hydrochloric acid with the amine, if it were split out by hydrolysis, would produce a much more exothermic effect than its union with water, the difference is not great enough to overcome the difference in energy expenditure required to separate the two substances, water or the amine, from the original compound.[1] To effect the hydrolysis would require so great an expenditure of energy that the reaction would be endothermic relatively to the one that actually takes place. Hence in this case the reaction would result in a less complete neutralization of the system than the one that occurs.

Tufts College, Mass.,
April 10, 1911.

REVIEWS.

The Relations between Chemical Constitution and Some Physical Properties. By Samuel Stiles, D.Sc., Fellow of University College, and Assistant Professor of Organic Chemistry at University College, London University. London, New York, Bombay, and Calcutta: Longmans, Green & Co. 1910. pp xiv + 583. Price, $4.

This is one of the text-books of Physical Chemistry edited by Sir William Ramsay, K.C.B., F.R.S.

In the preface the author says: "As indicated by the title, this volume does not exhaustively treat of the whole subject in question. For various reasons a few physical properties have been omitted from consideration, the more important being Crystalline Form, Optical Rotatory Power, Electric Conductivity, and Heat of Combustion. The relations between the first named of these properties and chemical constitution could not be fully understood without some general account of crystalline structure and the methods of measurement, so that a satisfactory treatment of this subject would occupy so much space as to require a separate volume. The relations between Constitution and Optical Rotatory

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[1] It is not intended to imply that the energy liberated by the union of the reagent with water or the amine, after the removal of that substance has taken place, does the work of separating these substances. This energy is furnished by the reagents and the heat supply. But the energy liberated in the two cases is a fair measure of the relative affinities of water and the amine for that acid.

Power, Electric Conductivity, and Heat of Combustion have been thoroughly dealt with in the volumes of this series entitled 'Stereochemistry,' 'Electrochemistry,' and 'Thermochemistry.' Some other physical properties, for example, Solubility, Dielectric Constant, and Magnetic Susceptibility, have been omitted because the relations between them and constitution are not yet sufficiently elucidated for special treatment."

Under the head "Mechanical Properties" there are three chapters which deal respectively with Capillarity, Viscosity, and Volume Relations. Under "Thermal Properties" the subjects of Specific Heat, Fusibility, and Boiling Point are treated of. Under "Optical Properties" come Refractive and Dispersive Power, Absorption of Light, Fluorescence, and Magnetic Rotating Power. Finally Anomalous Electric Absorption is dealt with under the general heading "Electrical Property."

The book is clearly written and is based upon the original sources to which abundant references are given.

In the concluding chapter occurs this passage which is worth quoting: "This problem of the nature of valency is undoubtedly the most important of those awaiting solution from the chemist. The opinion of chemists seems divided as to whether the electronic theory can be accepted or not. Against its adoption it is urged that the electron is nothing but a figment of the physicist's imagination, and that chemists can derive no real benefit from it. But it may be pertinently asked whether the atom is not equally a figment of the chemist's imagination, and are we to reject this too? At present, however, the electronic theory seems to be the only means by which there is any prospect of attaining further knowledge of the nature of valency, and this circumstance alone should be sufficient recommendation for a thorough trial. At any rate, if we reject it we have nothing else to offer as an adequate substitute."

The book is warmly recommended to students of chemistry whether they be young or old. I. R.

INTRODUCTORY NOTES ON QUANTITATIVE CHEMICAL ANALYSIS. By CHARLES WILLIAM FOULK, Professor of Analytical Chemistry in the Ohio State University. Second edition. Revised and enlarged. Columbus, O. 1910. pp. ix + 250. Price, $2.50.

The keynote of this manual is practical helpfulness to the beginning analyst. The author's aim is that of all good teachers of the subject, namely, to train their students to thoughtful, self-critical work, and the distinctive feature of these "Notes" is the large amount of descriptive and explanatory matter which is presented as bearing upon all analytical work, rather than upon any one procedure, or even to any group of methods. This material constitutes Part I, amounting to 129 pages, and is entitled "Principles of Chemistry and Manipulation in Quantitative Analysis." It is subdivided into introductory matter (glass-working, equipment, weighing and the balance), gravimetric analysis (sampling, precipitation, filtration, ignition, evaporation, management of work, note-books, and accuracy of analysis), and volumetric analysis (measurement of liquids, calibration, standard and normal solutions, titration and indicators).

"Practice Work in Quantitative Analysis" constitutes Part II, which comprises directions for the analysis of eleven substances and the preparation of some standard solutions. These directions are accompanied by explanatory notes bearing upon the particular determinations involved. With one exception, the materials analyzed are natural or manufactured products of commercial importance.

The attractiveness of this book lies in the candid, man-to-man fashion in which the author deals with his subject. This is particularly true of the sections on the "Accuracy of Chemical Analysis," in which the troublesome question of "check results" is admirably dealt with. A conscientious reader of Part I can hardly fail to gain an intelligent notion of the considerations which govern such matters as the choice of analytical methods and the amounts of materials to be taken for examination, to name only two of the important topics discussed. Whether a considerable proportion of a large class can be persuaded to read carefully, and assimilate, 129 pages of good advice is always a doubtful question, and will obviously depend largely on the pressure brought to bear upon the members of the class by the instructor. It may be questioned whether the treatment of certain topics (notably, the solubility-product principle) is adequate, and the suggestion (p. 57) that successive volumes of 800 to 900 cc. of water may be used to wash an aluminium hydroxide precipitate may be criticized, if subsequent determinations are to be made in the filtrate; but these are minor points in a mass of highly useful material, and the book is well worthy the attention of all thoughtful teachers.

H. P. TALBOT.

INTRODUCTION TO THE ANALYSIS OF DRUGS AND MEDICINES. An Elementary Handbook for the Beginner. By BURT E. NELSON, Chemist to the New York State Hospitals, The Department of Health, Board of Water Commissioners, etc. First edition. New York: John Wiley & Sons. 1910. pp. xii + 384. Price, $3.

In the preface the author states that the book is intended to furnish methods by which the student or analyst who is not specialized in drug chemistry may obtain information which is often desired by Health Departments, the State and the general public. The headings of some of the chapters are as follows: "Ultimate Inorganic Analysis," "Ultimate Organic Analysis," "Determination of Molecular Weights," "Common Radicles and Chemical Formulae," "Systematic Microscopical Drug Analysis," "Phamacological Methods," etc. From this it will be seen that the author attempts to cover within this small work several very large fields of work which bear more or less on the problem of the drug analyst. For this reason the statements are frequently so brief that they would be practically meaningless to any one but an advanced student and they are not sufficiently detailed to be of much service to him.

The chapter on pharmacological methods should certainly have been omitted, as in the reviewer's opinion it cannot be of service to any one, and the author could have devoted these pages far more profitably to further amplify other phases of the work. The same statement also applies to pages 93 to 96, wherein the author gives directions for the recognition of hydroxyl, carboxyl, methoxyl, ethoxyl, carbonyl, amino, amido, nitrile, imino, diazo, hydrazide, nitro, nitroso peroxide and iodoso groups—all within four pages.

The book would be of far greater service if it were more detailed and were narrower in its scope. A. S. L.

A TEXT-BOOK OF BOTANY AND PHARMACOGNOSY. By HENRY KRAEMER, Ph.B., Ph.D., Professor of Botany and Pharmacognosy in the Philadelphia College of Pharmacy. Illustrated with over 300 plates comprising about 2000 figures. Fourth edition, revised and enlarged. Philadelphia and London: J. B. Lippincott Co. pp. viii + 888. Price, $5.00.

This new edition of Kraemer's Text-Book is divided about equally between the subjects indicated in the title.

The first chapter deals with the great groups of plants, and in it the author undertakes to present their characteristics, relationships, reproductive processes and economic uses; this is rather a large order for the space devoted to it, and results in a condensed form of presentation.

Chapters follow on the outer and inner morphology of the higher plants, one on the classification of angiosperms, and a short chapter on drug cultivation. This part of the book is well illustrated. The idea of centrospheres in higher plants seems to die hard, for it is here again repeated with Strasburger's early cut.

In the section devoted to Pharmacognosy, each drug is described briefly and its names, habitat, range and principal constituents given. Allied products and plants are also mentioned. It seems rather unfortunate, however, that the medicinal action of the drug is in most cases omitted.

The chapter on powdered drugs is furnished with an identification key in which the main classification is according to color. The key is carefully worked out and illustrated and should prove of value to druggists who use the microscope.

The chapter on the crystallographic study of a number of drugs is new in this edition. It is illustrated by a number of pictures of microscopic crystals.

The book is well printed and illustrated throughout and will be welcomed by food analysts and druggists as a book of reference.

R. H. DENNISTON.

KRAFTGAS. Seine Herstellung und Beurteilung. Von. PROF. DR. FERDINAND FISCHER, Professor an der Universität Göttingen. Mit 186 Figuren im Text. Leipzig: Verlag von Otto Spamer. 1911. s. viii + 236. Preis, geh., M. 12; geb., M. 13.50.

The book discusses thoroughly the methods of testing and investigating power gases, the raw materials for their production and the theoretical considerations involved in their manufacture.

German generators are the ones chiefly described, although one finds those of Messrs. Solvay and Taylor. The book is, from this standpoint, more valuable to the European than the American. Scant attention is paid to the extensive use of blast-furnace gas for power in this country. Particularly interesting and opportune are the chapters upon Brown Coal, Peat, Wood, and Blast-Furnace Gases.

It is to be regretted that so good a book is furnished with so insufficient an index; a list of author's or patentees' names would be very helpful.

A. H. GILL.

VAN NOSTRAND'S CHEMICAL ANNUAL 1909. A Handbook of Useful Data for Analytical, Manufacturing and Investigating Chemists. Second issue. Edited by JOHN C. OLSEN, A.M., Ph.D., Professor of Analytical Chemistry, Polytechnic Institute, Brooklyn. New York: D. Van Nostrand Co. 1909. pp. xii + 580. Price, $2.50.

In this second edition of Van Nostrand's Chemical Annual the tables of the properties of the elements and of inorganic and organic compounds have been thoroughly revised and the table of gravimetric factors and their logarithms has been recalculated on the basis of the 1909 International Atomic Weights. Tables on the physical constants of the alkaloids and of essential oils and various other additions have been introduced. The reviewer has been using the book for some time and has found it uniformly accurate and up-to-date. The printing and binding are up to the Van Nostrand standard, the legibility procured by the large type and opaque paper more than compensating for the somewhat larger size of the book as compared with pocket reference manuals. The 108 pages, forming nearly one-fifth of the book, devoted to a list of the principal papers and books on chemical subjects published since the appearance of the first issue of the Annual, might, however, in the reviewer's opinion, be left out without much detracting from the value of the book, and the purchaser be given the benefit of the saving in the cost of production. C. A. R.

ANNUAIRE POUR L'AN 1911. Avec des Notes Scientifiques. Paris: Gauthier-Villars, Imprimeur-Libraire du Bureau des Longitudes. pp. vii + 761. Price, Fr. 1.50.

This little Annual (little in the size but not in the number and contents of its pages) is published by the Bureau des Longitudes. Every alternate year, tables of physical and chemical data are given, but 1911 happens to be an "off" year for these subjects and the present volume is devoted to astronomical, geographic and statistical data. Thus we find 73 pages given to the Gregorian, Julian, French Republican, Jewish, Turkish, Coptic and Chinese calendars, 20 to celestial phenomena during 1911, 184 to data on the solar system, 204 to geographical data, 8 to legal time in various parts of the world, 12 to French mortality tables, 88 to coins, weights and measures, 32 to interest tables, and 17 to meteorological data, chiefly for Paris. There are also appended reports on the 16th Meeting of the International Geodetic Association by H. Poincaré and on the Solar Eclipse of April 17th, 1912, by G. Bigourdon, an obituary of Bouquet de la Grye by H. Poincaré, and an address by the same author delivered at the funeral of Paul Gautier, December 9, 1909. C. A. R.

NITROCELLULOSE INDUSTRY. BY EDWARD CHAUNCEY WORDEN, PH.C., M.A., F.C.S. Over 8000 Patent and Literature References to the Work of over 2900 Different Investigators. Two Volumes, 324 Illustrations. New York: D. Van Nostrand Co. 1911. pp. xxxiv + 1239. Price, $10.00.

This work is styled in its sub-title "a compendium of the history, chemistry, manufacture, commercial application and analysis of nitrates, acetates and xanthates of cellulose as applied to the peaceful arts, with a chapter on gun cotton, smokeless powder and explosive cellulose nitrates," but the author has not been able to resist the temptation which presents itself to every student of chemical technology and which appeals most strongly to him who deals with an industry from the broadest scientific viewpoint, for he knows that his narration is not complete and that a true presentation of the development and existing conditions for any one industry cannot be made without a somewhat detailed account of the collateral and interdependent industries. Consequently the author deals not only with pyroxylin plastic substitutes and their various applications but he devotes much space to solvents and nonsolvents, fusel oil and the amyl alcohols, amyl acetates, natural, artificial and synthetic camphor and camphor substitutes, paint and varnish removers and turpentine substitutes, denatured alcohol, and other topics, giving the sources, methods of manufacture, properties and tests of most of these materials, and to this, for the information of manufacturers, adds a chapter on the transportation of explosives and inflammables, as regulated by the Bureau of the American Railway Association.

Considering the work as a whole, while it treats of most, if not all, of the applications of the cellulose nitrates, and of many of the industries based on these applications, with marked fulness of detail, yet the impression on reading is that the author focuses his attention on the proxylin plastic industries, which present in their treatment of the material, and applications of the products, a wide range of ingenuity, versatility, and usefulness and which are best exemplified in the composition of matter known under the copyrighted name of "celluloid." It may safely be said that this book gives the most detailed, precise and complete account of this industry thus far published. It is interesting, in view of popular opinion, to note that, in describing proxylin plastics, the author says: "When properly prepared, celluloid cannot be caused to explode by heat, friction, or percussion."

The text of this book is reinforced by most voluminous explanatory notes. Of the 1145 pages of text only 150 are free from notes and 31 of these are devoted to reprints of official documents. In some instances the explanatory, well digested notes cover nearly the whole page. While scientific authorities have been freely consulted and their results frankly presented without prejudice, the greatest stress, both in text and notes, is laid, as it should be for modern industries, upon patent literature. The descriptions of apparatus, methods, processes and products drawn from these literary sources is set forth with completeness, but a reader skilled in the art will observe that the author has exercised that discretion, when describing commercial operations, which good taste and justice to manufacturers demands.

In order that the wealth of information here collected may be made available the author gives a list of American and English Patents on pyroxylin plastics covering 19 pages; an index to U. S. and foreign patents covering all the industries treated of; an index of "authors;" an index of subjects; and a table of contents, with an extended list of abbreviations used, which is prefixed to each volume. The indexes include the notes as well as the text.

With these manifest evidences of painstaking care and industry in the preparation of this work one hesitates to criticize, yet it must be said that the text is at times so rough and involved that one is in doubt as to the author's meaning, and that, despite the careful research made by the author, he has sought to cover so broad a field that he has perforce failed to cover it completely, while slips such as "native Franklinite (zinc carbonate) plentiful in New Jersey" are to be expected.

In spite of these minor defects the treatise is most valuable to manufacturer, investigator and student and it must without doubt achieve the position of "authority" in the major topics of which it treats. CHARLES E. MUNROE.

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