THE BASIC PROPERTIES OF OXYGEN.

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During the last few years, Baeyer and Villiger[1] have published a number of interesting and valuable papers on the basic properties of oxygen. These investigators have produced compounds from oxygen bases, such as the ethers, alcohols and esters, and acids, such as ferrocyanic acid, and have explained their constitutions by assuming the tetravalency of oxygen (the oxonium theory of Collie and Tickle). These ferrocyanic compounds were formed generally by the addition of an aqueous solution of potassium ferrocyanide containing hydrochloric acid to the organic substance. A compound separated or crystallized out and the amounts of the organic constituent and of the acid were determined in the ordinary way.

If the ferrocyanic acid were attached to the oxygen base in the simplest way, four molecules of the latter should unite with one of the former. In many of the compounds described by Baeyer and Villiger, the combining ratio was not four to one. On this account, and the fact that water may have been present in their salts, I have made some experiments on the compounds of this acid with methyl and ethyl alcohols, acetone and ether. In this paper I shall give my reasons for believing that these compounds are not tetravalent oxygen compounds, and that with the alcohols we have merely alcohol of crystallization, while with ether and acetone solid solutions are formed.

One might criticize Baeyer and Villiger's choice of ferrocyanic acid for an investigation upon the basic properties of oxygen. True it is strong acid,[2] but its constitution is complex—perhaps not known with certainty. In addition it is a solid, so that additive compounds would naturally be regarded as acid with ether or alcohol of crystallization, unless the contrary were proved.

The ferrocyanic acid used in this investigation was prepared from a strong solution of potassium ferrocyanide by addition of hydrochloric acid and ether. The precipitate was filtered off and the ether removed in a vacuum. The acid was then dissolved and the precipitation repeated. After the third precipitation, the acid was dried for several weeks in a vacuum desiccator, care being taken to exclude the light. The various samples were slightly bluish and showed from 99.2 to 99.6 per cent. of acid when titrated with standard alkali and phenolphthalein. The other materials, alcohols, etc., were purified and dried in the ordinary ways.

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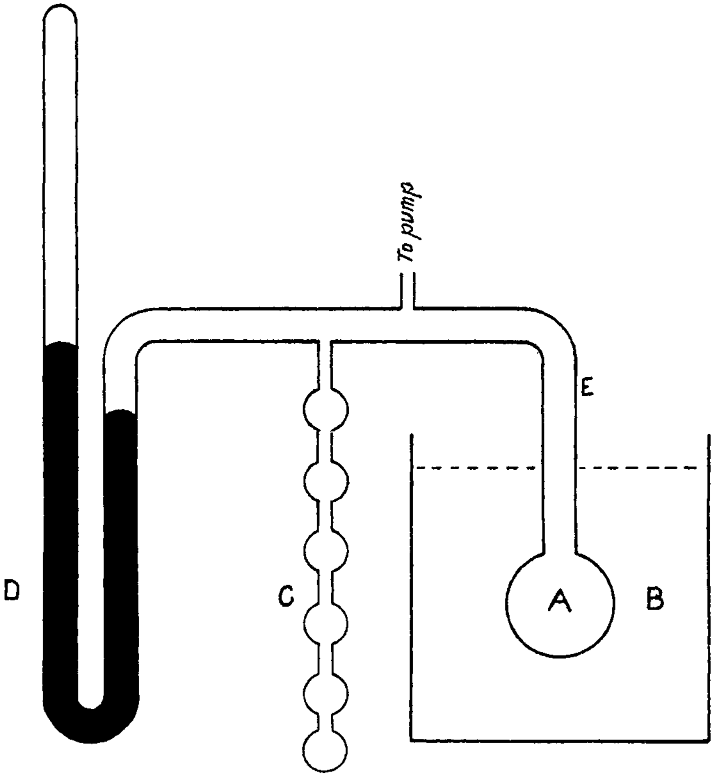
[1] Baeyer, Gesammelte Werke, p. 811. *Ber.*, **34**, 2679, 3612 (1901); **35**, 1201 (1902). Schmidt, Die basischem Eigenschaften des Sauerstoffs and Kohlenstoffs.

[2] Ostwald, *J. prakt. Chem.*, **32**, 308 (1885).

Experiments with Ether and Acetone.—The acid in contact with ether is insoluble but increases in volume with the evolution of a small but noticeable amount of heat.[1] For the composition of this compound, Browning gives 2 molecules of ether to one of acid, while Baeyer and Villiger find 2.7. Ether vapor at 35° C. passed over this substance arranged with Professor Richards's "bottling" apparatus gave about 2.3 molecules of ether to one of acid, but the complex had apparently a high vapor pressure so that the analyses varied widely. Attempts to prepare and dry this compound at low temperatures were unsuccessful; ether was removed by suction and the amount of acid found depended on the time and the method of drying used.

Now the ether or acetone absorbed by this acid is very different from the water or alcohol of crystallization retained by many salts, since the acid is insoluble in these liquids. Here a compound may be formed or we may have a solid solution. In the former case the vapor pressure



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[1] The compounds formed with the halogen acids and organic oxygen bases give out large amounts of heat. For example: $C_4H_{10}O + HBr = C_4H_{10}O, HBr + 85 \times$

will remain constant with constant temperature as long as any part of the compound remains undecomposed; in the latter the pressure will vary with the relative amounts of the two constituents.

These vapor pressures were measured in the apparatus shown in the figure, which is not drawn to scale. *A* is a large bulb into which the compound is placed with an excess of ether; it is then sealed to the tube E. The side tube *C* consists of ten or twelve bulbs, and *D* is a mercury manometer. The apparatus is attached to a Toepler pump, the bulb *A* cooled in liquid air, and when completely exhausted, the tube leading to the pump is sealed off. *A* is kept in a well-stirred water bath, *B*, provided with a small incandescent lamp and a magnetic regulator of the ordinary pattern, which maintains the temperature constant to 0.2°. The side tube *C* is water jacketed, and to prevent condensation of ether, the tube connecting *A* and *D* is wound with resistance wire through which a small current is sent. To diminish the amount of ether in *A* the water-jacket is removed and the lowest bulb cooled in liquid air. Ether distils over, and when a sufficient quantity has condensed, the bulb is sealed off with a small blowpipe flame. A dozen curves could be obtained in this way without opening the apparatus.

The results of one of the three series of experiments with ether, as successive portions are removed, are given in Table I and the curves are shown in Fig. 1. There *A* is the vapor pressure curve from Ramsay and Young's measurements. The points immediately above it are the vapor pressures of an excess of ether in contact with the acid, so that the ether-acid mixture must have contained a small amount of water introduced in sealing on the bulb. On removing portion of ether, the pressure falls and we obtain the curves B, C, D, E, F, and G. From the slope of the last curve it is clear that the rise of pressure with temperature is due principally to the expansion of vapor.

TABLE I.—ETHER.

A.		B.		C.		D.		E.		F.		G.	
Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.
8.5	260	18.0	377	13.6	290	17.7	328	10.6	119	14.0	103	15.0	71
19.9	427	26.0	525	25.0	459	22.0	386	20.8	220	18.0	135	21.5	97
22.5	471	30.3	621	33.5	621	26.7	451	25.4	277	25.5	200	32.6	163
27.0	557	....	...	....	...	33.0	566	30.6	337	32.5	282	....	...
29.0	599	....	...	....	...	....	...	....	...	....	...	....	...

These curves show that we have here a solid solution and not a compound, for even with substances having water of crystallization, such as the hydrated copper sulphate, the vapor pressure remains constant until $CuSO_4.5H_2O$ is completely decomposed; then the pressure drops suddenly to that of $CuSO_4.3H_2O$. No discontinuity of that kind can be noticed in the experiments with ether.

On mixing acetone and the acid, a sticky mass is first produced, but on rubbing in a mortar with more acetone the volume increases greatly and a little heat is evolved. Analyses of this compound, or one prepared by passing acetone vapor over the acid, gave unsatisfactory results: the amount of acid found depended on the time taken in drying the substance.

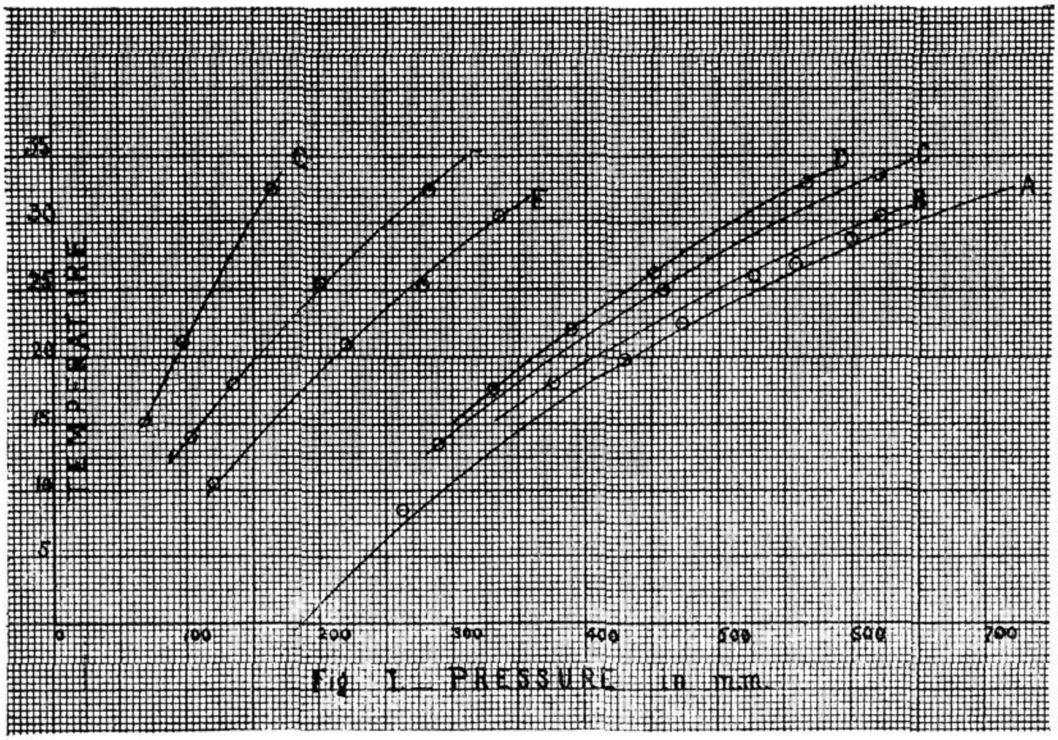

Fig. 1.—PRESSURE in mm.

The vapor pressures were measured in the apparatus previously described. In Table II. are given the measurements and in Fig. 2 the curves. *A* is the curve from Regnault's data, while the points lying near *A* are the observations made with an excess of acetone. *B*, *C*, *D*, and *E* are the curves obtained as successive amounts of acetone are removed. Here as in the experiments with ether there is no compound with a definite vapor pressure, and we must conclude that we have another case of solid solution.

TABLE II.—ACETONE.

A.		B.		C.		D.		E.	
Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.	Temp.	Pres.
17.0	155	19.4	152	22.0	161	21.7	140	14.5	35
19.2	170	29.2	250	31.8	238	30.0	195	20.0	55
25.9	230	38.4	381	37.5	299	39.8	270	29.2	86
34.6	331	48.6	551	43.0	344	44.6	323	41.0	178
39.5	402	....	...	....	...	....	...	45.5	215
48.7	562	....	...	....	...	....	...	....	...

Compounds with Methyl and Ethyl Alcohol.—A compound with ethyl alcohol containing 3 molecules of alcohol has been prepared by Baeyer and Villiger. No attempt to reproduce this substance has been made, but another compound has been prepared. The acid dissolves readily in alcohol, and if the solution is cooled crystals separate out. These melt sharply at —45°, and when dried by suction at —80° give 35.7[1] per cent. of acid. $HFe(CN)_6 10C_2H_6O$ contains 32 per cent, and $H_4Fe(CN)_6 8C_2H_6O$ 37 per cent. acid.

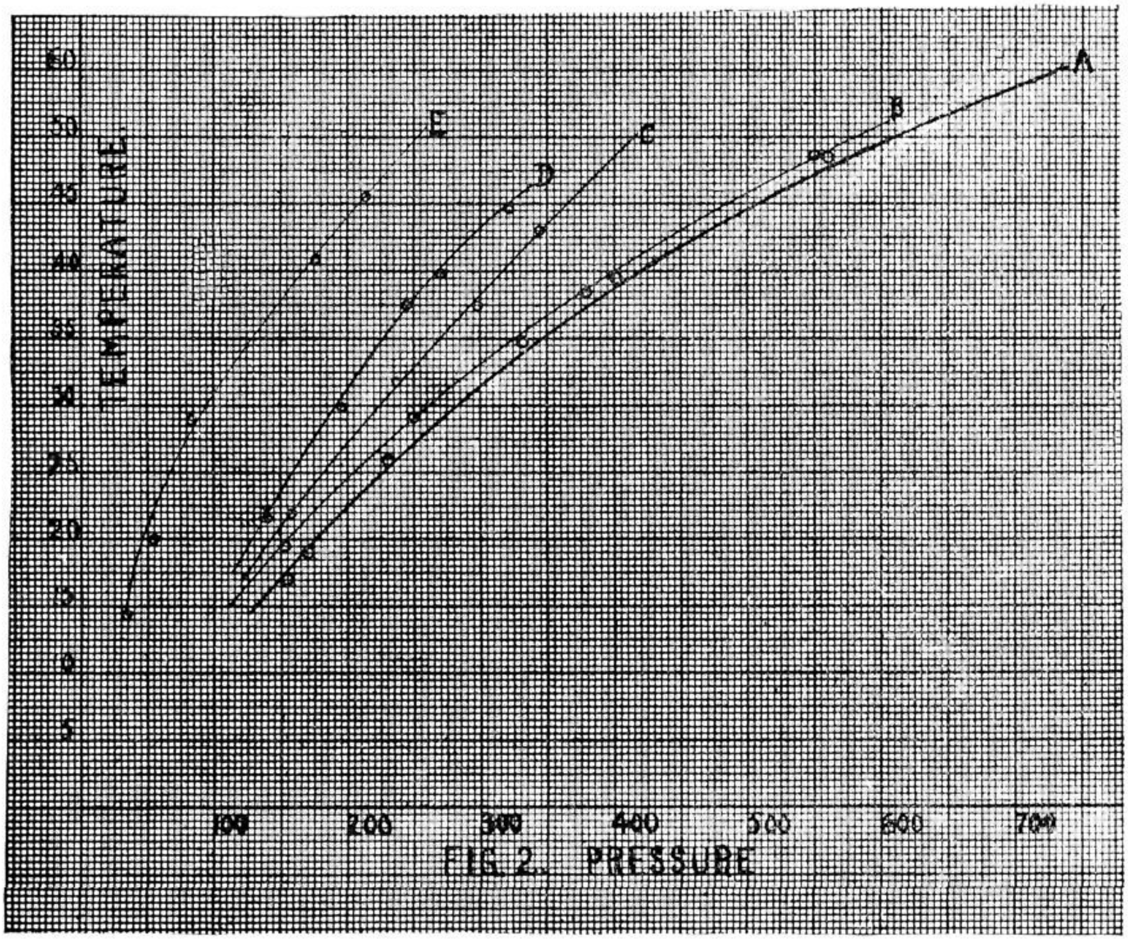

FIG. 2.

Similarly, crystals[2] melting at —33° C. were obtained with methyl alcohol and these contained 37 per cent. of acid. $H_4Fe(CN)_6 10CH_4O$ has 40 and $H_4Fe(CN)_6 12CH_4O$ 36 per cent.

Here we have two alcoholates melting at low temperatures consisting of about ten molecules of alcohol to one of the acid, which are much more complex than those described by Baeyer and Villiger. There is nothing in their properties to differentiate them from salts with water or alcohol of crystallization. With decreasing temperatures the complexity increases, just as in the case of many hydrated salts among which the system ferric chloride-water is a striking example.

On account of the reduction of the ferrocyanic acid no determinations of the solubility change in alcohol with temperature were made. Were this possible, these two-component systems could be mapped out, and

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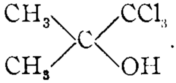
[1] Sample 1, 35.7 acid; Sample 2, 35.8.

[2] Four specimens containing from 35 to 40 per cent. acid were analyzed.

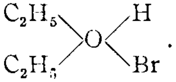
the temperatures at which the various alcoholates are in equilibrium with one another and the acid could be fixed.

However, many investigations of this nature have been carried out with alcohol, ether, acetone, etc.; alcoholates of lithium chloride are well known, and potassium hydroxide gives a compound, $KOHC_3H_6O$. Menschutkin[1] has recently studied the system $CaCl_2$-CH_3OH and has prepared two compounds containing three and four molecules of alcohol, while with magnesium bromide and ether he finds two crystalline substances with one and two molecules of ether. The compounds with ferrocyanic acid do not seem to differ from many salts which crystallize with water and other oxygen bases, and they throw no new light on the existence of tetravalent oxygen. A higher valency of oxygen than two may be necessary for an explanation of the constitution of compounds containing water of crystallization, but such a theory gains nothing from the experiments with hydrogen ferrocyanide and methyl and ethyl alcohols.

Compounds of the Halogen Acids and Oxygen Bases.—Many combinations of the halogen acids with organic substances containing oxygen have been described. In these compounds, following Friedel, a tetravalent oxygen atom has been assumed, and the view that these additive compounds differ essentially from the so-called molecular compounds has been expressed. With ethyl ether and hydrobromic acid, experiment has failed to show more than one proportion ($C_4H_{10}OHBr$, M.P. —40°) in which these constituents unite between —85° and —40°. From the low melting points of the acid and the ether (—86 and —117) the substance can not be a cryohydrate. Further, salts containing alcohol or water of crystallization liquefy below or between the melting points of the constituents. This is not the case with ether hydrobromide; the melting point is many degrees above that of either constituent. The separation of a solid substance from the liquids acetone and chloroform was looked on by Willgerodt[2] as proof of the existence of a true chemical compound, and subsequent experiment gave the constitution



In the same way we may view the production of a solid from the liquids ether and hydrogen bromide as the formation of a chemical compound and give to it the constitution



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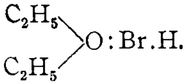
[1] *Z. anorg. Chem.*, 49, 34 (1906); 49, 207 (1906); 52, 9 (1907).

[2] *Ber.*, 14, 2456 (1881).

This formula is borne out by the behavior when electrolyzed in hydrobromic acid solution. The ether under an electrical stress moves toward the cathode, which would not be the case were the constitution



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O:Br.H.$$

We may compare a combination of this type (methyl ether hydrobromide) with a compound such as ammonium hydrosulphide, which is admitted to be a true chemical compound.

	M. p.	B. p.		M. p.	B. p.
Ammonia	—90	—35	Methyl ether	—120	—26
Hydrogen sulphide	—85	—60	Hydrobromic acid	—86	—68
Compound	12 0	..	Compound	—22	..

The difference between the two compounds seems merely one of degree. Both show high vapor pressures at their melting points, but in the case of the ether hydrobromide substitution as well as dissociation takes place.

In this paper I have attempted to show that the additive compounds of methyl and ethyl alcohol with ferrocyanic acid were probably molecular compounds, while ether and acetone yield, not compounds, but solid solutions. To study each of the numerous complexes described by Baeyer and Villiger is impossible, but I hope in the future to examine a few others as well as some of the compounds produced by the Grignard reaction and by Collie and Tickle.

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During the past year I have made some compounds of the halogen hydrides with organic bases for particular purposes, and as several of these have not been described I shall give their composition here.

Acetic Acid Compounds.—Acetic acid dissolves in liquefied hydrobromic and hydriodic acids with considerable heat evolution. forming viscous liquids from which crystalline substances precipitate on standing. The hydrobromic acid complex melts at 5°, and is difficult to purify, various analyses giving from 46 to 49 per cent. hydrobromic. Tshitshibabin[1] has obtained a compound, $(C_2H_4O_2)_2HBr$, melting at 7°–8°; it contains 40 per cent. of acid.

The hydriodic product melts at a much lower temperature (—50°) and showed in different samples between 59 and 70 per cent. acid. Two molecules of the halide acid may unite with either two or three molecules of acetic acid.

Methyl Ethyl Ether Compounds.—The ether was prepared by the action of sodium methylate on ethyl iodide. It was fractionally distilled and the portion boiling between 10° and 11° was used.

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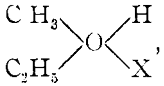
[1] *J. Russ. Phys. Chem. Soc.*, **7**, 1058 (1906).

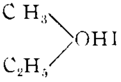
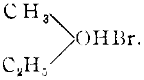
This ether dissolves readily in the hydrogen bromide or iodide with the development of a large quantity of heat. White crystals separate out, which melt sharply at —30° in the case of hydrobromic acid compounds, and at —22° in the other. One molecule of acid unites with one molecule of the ether—a result to be expected from the composition of di-methyl and di-ethyl acid compounds. These compounds, if the oxygen is tetravalent, have the composition



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}H\\X\end{matrix},$$

and here the oxygen is asymmetric. Attempts to separate these compounds into their optically active isomers have not been successful.

The melting points of the various ether compounds with hydrobromic and hydriodic acids are given in the following table:

Compounds.	M. P.
$(CH_3)_2OHI$	—15
$(CH_3)_2OHBr$	—22
$(C_2H_5)_2OHI$	—18
$(C_2H_5)_2OHBr$	—40
 $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!OHI$	—22
 $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!OHBr$	—30

McGILL UNIVERSITY, MONTREAL,
February, 1908.

A NEW METHOD OF SEPARATING LITHIUM CHLORIDE FROM THE CHLORIDES OF THE OTHER ALKALIS, AND FROM THE CHLORIDE OF BARIUM.

BY LOUIS KAHLENBERG AND FRANCIS C. KRAUSKOPF.

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It is well known that the separation of lithium from the other alkali metals presents considerable difficulty. In his investigations of the mineral water of Karlsbad, Berzelius[1] sought to separate lithium from sodium and potassium by adding phosphoric acid to the solution and then neutralizing with sodium carbonate in slight excess. On evaporating this alkaline solution to dryness and then extracting with cold water a residue was obtained, which he regarded as a double phosphate of sodium and lithium, which, upon ignition, yielded the pyrophosphates of sodium and lithium in equimolecular proportions. Later Rammelsberg[2] demonstrated that upon evaporating the alkaline solution prepared accord-

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[1] *Pogg. Ann.*, 4, 245 (1825).

[2] *Ibid.*, 66, 79 (1845).