The monohydrate does not possess this property to any degree comparable to the hexahydrate. But very light gray colored residues were produced under circumstances which produced the black residues with the hexahydrate.

It seems reasonable, therefore, that a substitution of these gaseous carbon compounds might be made for the water in the structure of complex hexahydrate. Higher temperatures would cause the firmly bound carbon compound to decompose and leave graphitic carbon which, upon further ignition, is extremely difficult to oxidize.

The authors wish to acknowledge their indebtedness to Professor Paul F. Kerr of the Department of Geology, Columbia University, for the x-ray work which appears in this paper.

Summary

1. The luminescence or flash during the ignition of magnesium ammonium phosphate hexahydrate and of magnesium ammonium phosphate monohydrate is due to the rise of temperature caused by the large quantity of heat liberated when the amorphous form of $Mg_2P_2O_7$ crystallizes.

2. The magnesium ammonium phosphate hexahydrate during the process of losing water of hydration in the early stages of ignition possesses the property of attaching firmly within its complex structure certain gaseous organic compounds, if present, which later break down and leave graphitic carbon.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Sorption of Organic Vapors by Resinous and Cellulosic Materials

BY CLARENCE H. WINNING AND JOHN WARREN WILLIAMS

The objects of a recent sorption balance study of the behavior of glyceryl phthalate resins in the presence of acetone and methyl alcohol vapors were stated to be five-fold: (1) to determine the form of the sorption isotherms at several temperatures and to interpret the curves in terms of the porous structure of the resin; (2) to determine the heat of the sorption processes by the comparison of two isotherms; (3) to make an estimate of the average pore size from the sorption behavior in the neighborhood of saturation; (4) to study the changes in structure produced by variations in the curing process to which the resin has been subjected; (5) to study the reversibility of the sorption process. The results of this study[1] were so interesting that it was decided to extend the work to other artificial resins, to several

[1] Winning and Williams, *J. Phys. Chem.*, **36**, 2915 (1932).

natural resins and to certain derivatives of cellulose, using the vapors of ethyl ether and chloroform as sorbate molecules.

The apparatus used was a McBain–Bakr balance, adapted to the sorption of vapors by powdered resin samples. It is completely described in the earlier article. Except for insignificant details the experimental procedure used was the same as that already described. Its particular advantage lies in the fact that it permits a continuous and complete sorption and desorption experiment to be made without disturbing the sorbent in any way, both with respect to the equilibria attained at the several partial pressures and to the rate at which these equilibrium values are approached. At the same time any effects of a true hysteresis will probably be recognized as readily by this method as by any other of procedure. The time allowed for the attainment of equilibrium was extended in certain cases to two full days; in the majority of cases, however, less time was required.

Experimental

Materials Used.—The glyptal resin spoken of in this article was prepared from glycerin and phthalic anhydride according to directions previously given. It was not "cured," and would therefore correspond to what has been called Resin I in the earlier article.

Phenolphthalein benzoate resin was prepared following the directions recently given by Zelinsky and Maksorow.[2]

A method of Lilienfeld[3] was used in the preparation of the benzyl cellulose. The material was heated in an evacuated tube for two days at 160 ° to remove absorbed liquid.

The cellulose acetate material was prepared by an acetylation process which results in a complete solution of the product.

As samples of natural products resins described as Pontianic Borneo and Congo fossil were used.

The organic liquids used, chloroform and ether, were subjected to rigorous purifications before being sealed into the sorption chambers.

TABLE I(a)

DATA FOR 35° ISOTHERMS—CHLOROFORM VAPOR

	Amounts sorbed per gram (x/m)			
p_x/p_s	Glyptal	Phenolphthalein benzoate	Benzyl cellulose	Cellulose acetate
0.202	0.243	0.151	0.088	0.176
.334	...	.163	.132	.239
.508	...	.381	.212	.367
.662	.257	.723	.331	.504
.817	.418	...	...	.765
.838	...	1.545	.914	...
.614	.350	0.585	.301	.563
.202	.310	.234	.097	.250

TABLE I(b)

DATA FOR 50° ISOTHERMS—CHLOROFORM VAPOR

	Amounts sorbed per gram (x/m)			
p_x/p_s	Glyptal	Phenolphthalein benzoate	Benzyl cellulose	Cellulose acetate
0.116	0.003	0.033	0.051	0.074
.191	.008	.046	.067	.109
.318	.024	.080	.100	.173
.468	.080	.227	.160	.270
.668	.133	.677	.292	.436
.845	.394	1.432	.848	.737
.572	.295	0.473	.244	.463
.265	.270	.214	.107	.256
.116	.253	.168	.060	.154
.000	...	...	.000	.007

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(2) Zelinsky and Maksorow, *Ind. Eng. Chem.*, **24,** 63 (1932).

(3) Lilienfeld, U. S. Pat. 1,858,019.

TABLE II

DATA FOR 35° ISOTHERMS—ETHER VAPOR

	Amounts sorbed per gram (x/m)			Amounts sorbed per gram (x/m)	
p_x/p_s	Congo fossil	Pontianic Borneo	p_x/p_s	Congo fossil	Pontianic Borneo
0.238	0.036	0.029	0.935	0.810	0.705
.326	.056	.056	.693	.218	.210
.450	.063	.080	.498	.132	.131
.572	.102	.117	.361	.100	.092
.693	.221	.210	.238	.083	...

Data and Results.—The results of representative experiments are presented in the form of tables and graphs.

Discussion

The Sorption and Desorption Processes.—High molecular weight substances of the type considered in this article are frequently assumed to have practically no permanent interspaces within the structural framework. They should then take up vapors by processes other than condensation unless these adsorption processes result in a partial resolution into the constituent molecules. The sorption curves for acetone and methyl alcohol on glyptal could be divided into three parts. In the first of these regions the highly polar sorbate molecules were able gradually to overcome strong cohesive forces, thereby penetrating the structure. Once the sorbate molecules have penetrated the structure the equilibrium value for the amount adsorbed is attained more readily and the isotherm becomes parallel to the pressure axis, indicating the completion of a process which we have assumed to be the filming of the structural units. As the partial pressure of the sorbate is further increased, a limited swelling takes place and the capillary spaces formed become filled with condensed liquid. Thus the process of adsorption is followed by one of condensation within the pores which have been opened up.

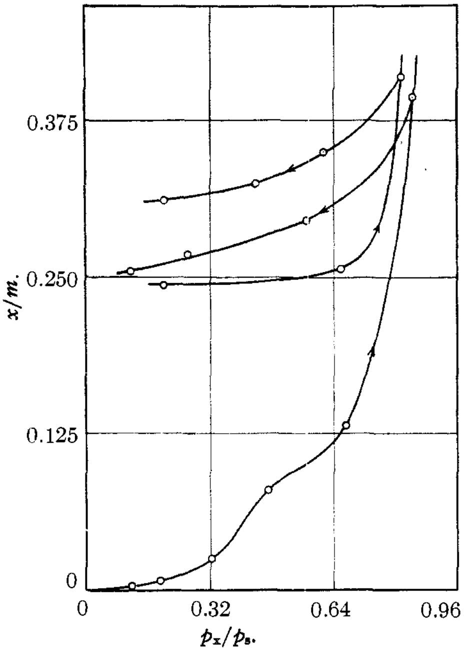

Fig. 1.—Glyptal–chloroform, 35 and 50° isotherms.

In the extension of the work to other sorbents and to other sorbate materials it was found that no two of the systems behaved exactly alike, yet in certain cases marked similarities in sorption and desorption curves were evident. A sample of "uncured" glyptal resin was found to take up chloroform vapor less readily than either acetone or methyl alcohol at the lower vapor pressures, but the three sorption regions described above are again recognizable in the 50° isotherm (Table I, Fig. 1). The adsorption process is an exceedingly slow one. This is probably to be accounted for on the basis of a closely knit structure which makes the inner surface areas difficultly accessible to the vapors of a larger molecule like chloroform, for it is believed that our experimental conditions preclude the necessity of a displacement of strongly adsorbed gases from the surfaces. The desorption process is irreversible to a marked extent, even far into the so-called condensation region. It is difficult to account for the tenacity with which the chloroform vapors are held, especially in the region where large amounts of vapor have been taken up and the uncured glyptal has assumed the appearance of a semi-fluid mass. A restrained diffusion would seem to furnish the most likely explanation, in which case experiments over much greater periods of time would undoubtedly improve the situation.

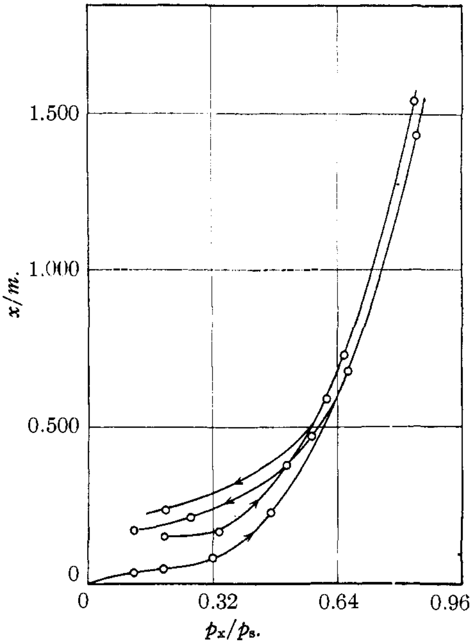

Fig. 2.—Phenolphthalein benzoate–chloroform, 35 and 50° isotherms.

The phenolphthalein benzoate resin, one of a series of phenolphthalein resins prepared by Zelinsky and Maksorow, was chosen as typical of a substance believed to have properties intermediate between the amorphous resins and those materials which are characterized by some regularity in structure. It takes up chloroform vapor in a normal way (Table I, Fig. 2), the sorption isotherm having the typical "S" shape which is so characteristic of a swelling gel. After completion of the 50° isotherm the same sample was used for experiments at 35°. It will be observed that at this temperature the sample did not begin to increase in weight until a partial pressure of 0.3 was reached.

The chloroform sorption and desorption data for the benzyl cellulose resin (Table I, Fig. 3) are interesting because of their resemblance to those which are presented for cellulose acetate using chloroform as sorbate (Table I, Fig. 4), and to those which have already been considered in the earlier article where acetone and methyl alcohol vapors were taken up by this ester. In all these cases closed sorption and desorption cycles are established. However, the hysteresis is much less marked with benzyl cellulose and it is possible to construct an equilibrium curve by interpolation, from which certain thermodynamical calculations seem justified. In this way information with regard to the sorption process in the region of the higher partial pressures for substances of cellulosic nature may be obtained. It should also be pointed out that the benzyl cellulose is much more readily disintegrated by chloroform vapors than is cellulose acetate. In this respect the ether is similar to an uncured glyptal. It is generally true that the sorption and desorption processes approach apparent equilibrium at a more rapid rate in the case of the cellulosic materials studied than is the case with the resins.

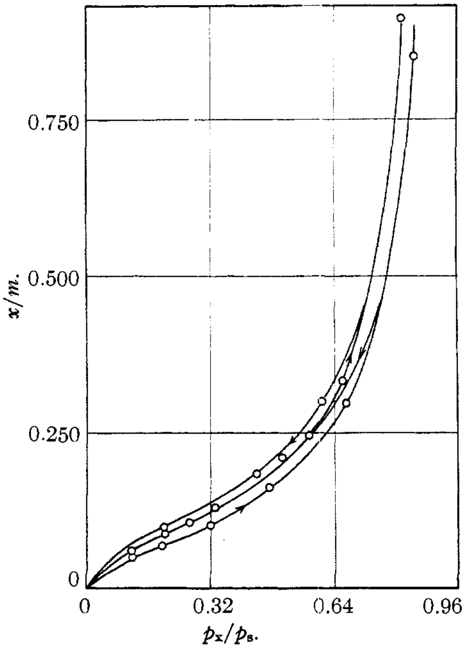

Fig. 3.—Benzyl cellulose–chloroform, 35 and 50° isotherms.

The sorption of ether vapor by the natural resins (Table II, Fig. 5) closely resembles that of acetone by cured glyptal resins. This resemblance suggests a similarity in structure. These natural resins are fossilized or aged to different degrees. The more mature resin (Pontianic Borneo) offers the greater resistance to the penetration of the vapors in the region of low partial pressures, presumably because of a more compact structure. The sorption and desorption processes are completely reversible in the higher partial pressure areas.

Irreversibility of the Sorption.—In no system investigated did we find the sorption and desorption processes to be completely reversible. In certain cases they approached reversibility when the partial pressures corresponded to the "capillary condensation" region. But if one subjects a sample of uncured glyptal resin to the action of chloroform vapor, the sorption and desorption processes are not at all reversible, even in the region of extremely high partial pressures. This will be evident from an inspection of Fig. 1. The 35° isotherm was determined using the same sample that had been used previously at 50°. Reduction in partial pressure for a period of several days did not serve to lower the vapor content to any appreciable extent.

On the basis of the hysteresis behavior, the substances studied may be divided into two classes, those which give a closed hysteresis cycle and those which apparently do not return to their original condition no matter how rigorous the evacuation treatment. Of the substances investigated, glyptal, phenolphthalein benzoate, and the natural resins did not return to their original weight. In agreement with Urquhart,[4] with Sheppard and Newsome[5] and with others who have studied the sorption of water vapor by cellulose derivatives, these materials were found to complete a cycle upon desorption whether acetone, methyl alcohol, or chloroform vapors were used in the experiments. The hysteresis cannot be entirely accounted for on the basis of the theory of the curvature of the liquid meniscus in the capillary spaces,[6] nor does its explanation on the basis of an interference of air or water with the wetting and filling of the pores seem satisfactory. It must be bound up in some way with the interaction between the active parts of the surface of the structural units and the molecules approaching these surfaces.

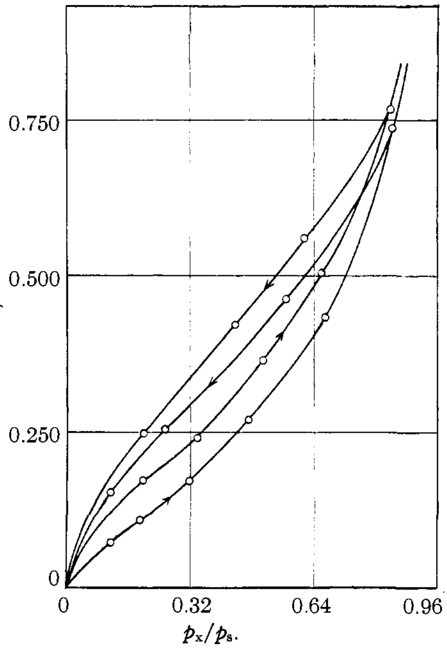

Fig. 4.—Cellulose acetate–chloroform, 35 and 50° isotherms.

The difference between the closed cycle type of hysteresis (cellulose derivatives) and that in which the desorption process fails to reduce the amount of vapor adsorbed to extremely small quantities at the very low partial pressures seems to be a real one, probably to be explained in terms of a difference in the forces which bind the liquid to the solid. Thus, while it was not considered safe to resort to an interpolation process to locate equilibrium curves for thermodynamic calculations in the case of the cellulose acetate, such a treatment has proved quite satisfactory in the

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(4) Urquhart, *J. Textile Inst.*, **20**, 125T (1929).

(5) Sheppard and Newsome, *J. Phys. Chem.*, **33**, 1817 (1929).

(6) See, for example, Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

case of the glyptal,[1] phenolphthalein benzoate and natural resins. The data for the benzyl cellulose sorption could be treated in this manner only because the area of the hysteresis cycle was small. Such a procedure is not without real experimental justification in the case of the resins because desorption experiments carried out over very greatly extended periods of time decrease the observed hysteresis to a certain extent. This is clearly indicated by the arrow in Fig. 3 of the earlier article. Usually the hysteresis area does not extend far into the region of capillary condensation; furthermore, it is greatest at the infinitely small vapor pressures.

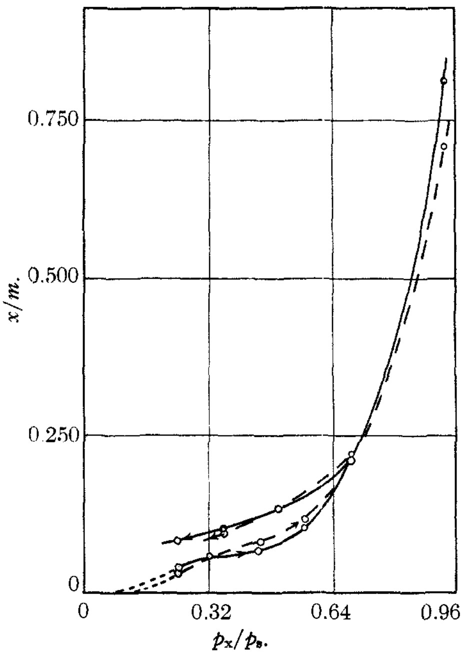

Fig. 5.—Ether vapor, 35° isotherms: Congo fossil————; Pontianic Borneo— — —.

A tentative explanation for the difference in the two kinds of hysteresis may be suggested if it can be assumed that the build of a gel material of the type considered in this article is predetermined by molecular orientations in the solution form. In general it seems safe to consider that elongated and regularly shaped units in the sol form may lead to the formation of an orderly and sensibly reproducible structural arrangement in the gel form, while odd-shaped molecules may be expected to give rise to accidental packings as the gel is again formed. The swelling of a gel may be explained by saying that either the forces holding the micelles together to form the massive material, or the forces causing the aggregation of molecules (or both, as the case may be), are overcome as the sorbate is able to penetrate more and more deeply. The sorption process is described as one in which first the structural units (molecules) are filmed, and then a condensation takes place in the voids or capillaries formed by the continued penetration of the sorbate. There is, therefore, a definite tendency toward a solution process. As the sorbate is removed from a system the reassociation of molecules may be such as to permit its eventual complete removal if the arrangement is a regular, and, as it was in the cases investigated by us, a less closely knit one; or it may be such as to effectively block and trap relatively large amounts of the sorbate due to random arrangements of molecules which may have different sizes as well as irregular shapes. Also, it is a recognized fact that in the study of the energetics of the sorption processes the distances between adsorbing surfaces and sorbate molecules are of fundamental significance in determining the relative importance of the adhesive and cohesive forces which result. A regular arrangement would seem to favor cohesion between adsorbing surfaces while in a random arrangement the adhesive forces could not be so completely overcome because the distance between adsorptive surfaces would always be variable, thus preventing practical return to the vapor-free or original state. Experiments designed to test this suggestion are now being made.

Thermodynamics of the Sorption Process.—Another of the methods by which there may be made available information with regard to the sorption processes at the solid–vapor interface is a study of the heats of the sorption. Provided the assumption can be made that the available solid surface remains constant in area during the adsorption, the affinity of such a surface which already contains the amount x of adsorbed vapor for the molecules of the vapor is

$$-\Delta F = RT \ln (p_s/p_x)$$

The total heat of wetting, $-\Delta H$, may therefore be determined using the Gibbs–Helmholtz equation

$$\Delta H = \Delta F - T(\partial \Delta F/\partial T)_x$$

Performing the operation indicated and integrating

$$-\Delta H = \frac{2.3\ RT_1T_2}{T_2 - T_1}\left(\log \frac{p_{x2}}{p_{x1}} - \log \frac{p_{s2}}{p_{s1}}\right)_x = -\Delta H_1 + \Delta H_2$$

The first term on the right side of this equation is the differential heat of adsorption and the second term, which is independent of the amount adsorbed, is the heat of vaporization of the liquid being condensed in the capillaries.

At low values of partial pressure the magnitudes of $-\Delta H$, and therefore of the differential heats of adsorption, may be very high. Our data are sufficient to show that as the amount of vapor adsorbed becomes greater $-\Delta H$ approaches zero because the value for the differential heat of adsorption approaches that of the latent heat of vaporization of the liquid being taken up by the solid material. This is shown by the data which have been collected to form Table III. The latent heat of vaporization for chloroform at its boiling point is 58.8 calories per gram.[7] The value calculated to 42.5° will be slightly more than 3 calories larger, or approximately 62 calories. The last column of both parts of Table III indicates a differential heat of adsorption which is only slightly larger than this value, suggesting that after the adsorption on the surface of the structural units of the materials has been completed the gel structure is opened up by a limited swelling and a condensation of the vapor takes place in the capillaries formed in this manner.[8] These data may therefore be considered to

(7) Mathews, THIS JOURNAL, **48**, 562 (1926).

(8) Peirce, *J. Textile Inst.*, **20**, T133 (1929).

indicate the importance of the process of condensation to liquid in the region of higher partial pressures.

TABLE III(a)[a]

CHANGE IN HEAT CONTENT DURING SORPTION PROCESS. BENZYL CELLULOSE RESIN—CHLOROFORM VAPOR

Calculations Made from Equilibrium Curves Determined by Interpolation

x/m	p_x/p_s (35°)	p_x (35°), mm.	p_x/p_s (50°)	p_x (50°), mm.	$-\Delta H_1/g.$
0.100	0.223	67.2	0.278	146.2	86.3
.150	.368	110.9	.420	221.0	76.5
.300	.620	186.8	.660	347.2	68.8
.450	.715	215.4	.757	398.2	68.2
.600	.762	229.6	.805	423.4	67.9
.750	.794	239.2	.836	439.7	67.6
.900	.816	245.9	.854	449.2	66.9

TABLE III(b)

CHANGE IN HEAT CONTENT DURING SORPTION PROCESS. PHENOLPHTHALEIN BENZOATE RESIN—CHLOROFORM VAPOR

Calculations Made from Equilibrium Curves Determined by Interpolation

x/m	p_x/p_s (35°)	p_x (35°), mm.	p_x/p_s (50°)	p_x (50°), mm.	$-\Delta H_1/g.$
0.300	0.428	129.0	0.458	240.9	69.3
.450	.547	164.8	.574	301.9	67.2
.600	.614	185.0	.643	338.2	66.9
.900	.712	214.5	.743	390.8	66.6
1.200	.782	235.6	.812	427.1	66.0
1.500	.832	250.7	.858	451.3	65.2

[a] These tables contain data which are entirely analogous to those of Table V of the previous article [Winning and Williams, *J. Phys. Chem.*, **36**, 2915 (1932)]. The data of the last column of this Table V are values calculated per gram of sorbent; therefore the word "mol" was inadvertently inserted.

The authors desire to express their appreciation to the Research Committee of the University of Wisconsin for substantial aid.

Summary

1. A balance of the McBain-Bakr type has been used to study the sorption of chloroform vapor by samples of glyptal, phenolphthalein benzoate, benzyl cellulose and cellulose acetate maintained at 35 and 50°. The sorption of ether vapor by samples of two natural resins maintained at 35° has also been investigated.

2. The sorbent materials may be characterized as typical swelling gels. As vapors continue to be taken up by them, the first process of surface adsorption is followed by a physical process of condensation of sorbate in capillary spaces or voids. These capillaries have been opened up after the structural units, probably molecules, have been completely filmed.

3. The hysteresis behavior of the resinous materials is different from that of the two cellulose derivates. An attempt is made to account for this difference on the basis of structural considerations. Regular

arrangement in build is believed to favor practically complete removal of sorbed vapors at extremely low partial pressures while random arrangement may lead to conditions which result in retention.

4. The heats of the several sorption processes have been calculated from the free energy changes, and their temperature coefficients.

MADISON, WISCONSIN RECEIVED APRIL 25, 1933
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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Potential of the Silver-Silver Iodate Electrode at 25°

BY J. N. PEARCE AND VERDA I. WIRTH

Any slightly soluble salt of a metal may form, potentially, a good electrode, provided the electrode is perfectly reversible and the metallic salt is stable in solution. The present paper gives briefly the results obtained from a study of the silver-silver iodate electrode.

Materials and Apparatus.—The silver crystals used in the preparation of the electrodes were formed by the electrolysis of a hot, concentrated solution of pure silver nitrate, using a platinum wire cathode and a pure silver anode, surrounded by a porous cup. A current of five to ten amperes gave uniform, well-defined crystals which were free from amorphous silver.

Silver iodate was prepared by adding a dilute solution of pure silver nitrate slowly and with rapid stirring to a large volume of a dilute solution of potassium iodate. The precipitate was washed free from excess salts and dissolved in a pure concentrated solution of ammonium hydroxide. The ammonia was allowed to evaporate spontaneously, leaving the iodate in the form of fine white crystals.[1] These were washed thoroughly and stored under conductivity water until used.

All other chemicals were carefully purified by approved methods. All solutions were made on the weight molal basis in conductivity water.

The experimental data recorded in the following tables are the mean potential values obtained from three to five cells, each containing three to five individual electrodes. While the calomel electrodes attained equilibrium quickly, the iodate electrodes required four or five days. The deviations of the potentials of the different electrodes in any single iodate half-cell did not exceed 0.05 mv., and the mean deviation of duplicate half-cells containing potassium iodate did not in any case exceed 0.2 mv.

The determination of the potentials of the iodate electrodes involved the measurement of electromotive forces of cells, with ion transference, of the type: Hg, Hg_2Cl_2, KCl (0.1 *m*), KIO_3 (0.1 *m*), $AgIO_3$, Ag. The half-cells were connected by a modified form of the Lamb and Larson[2] flowing junction device. The liquid junction potentials were calculated by means of the relation used by Lewis and Sargent,[3] namely

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(1) Greensfelder and Latimer, THIS JOURNAL, **53**, 3813 (1931).

(2) Lamb and Larson, *ibid.*, **42**, 239 (1920).

(3) Lewis and Sargent, *ibid.*, **31**, 363 (1909).