4. The ordinary thermodynamic formula for the electromotive force of a concentration cell with transport ignores the transport of water. If this be taken into account the transport number involved is the true and not the Hittorf number.

5. Emphasis is laid upon the fact that activity measurements give the activity of the unhydrated ion. An increase in the fraction of ions not hydrated gives the simplest explanation of the increase of activity coefficients in concentrated solutions.

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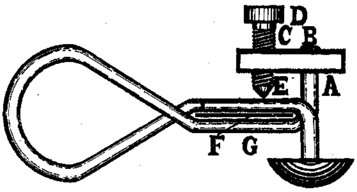
NOTES

A Screw Modification of the Mohr Pinch Clamp.—Although the use of a Mohr buret is often made imperative in volumetric work, no satisfactory pinch clamp has ever been devised to allow dropwise delivery of solutions from a buret of this type. The accompanying sketch shows the details of a pinch clamp designed to fill this need. It may easily be made from an ordinary Mohr clamp, and has an advantage over a screw clamp in that only one hand is required for its manipulation.



Into a brass plate 3 mm. thick, 1 cm. wide, and 2 cm. long 2 holes, B and C, are drilled and then tapped. The wire A leading up from the jaws of the clamp is threaded, screwed into the plate through B, and then brazed or soldered securely in the position shown in the figure. A large-headed brass screw D is then screwed through C until its pointed end E just touches the top of plate F when the clamp is pressed just hard enough to allow liquid to pass in drops through the rubber tube between plate F and wire G. Of course, by screwing D further it is possible to secure any other desired rate of flow.

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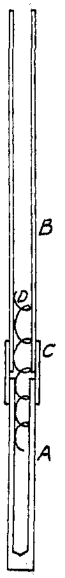
Received February 10, 1923

Gas Electrode.—A convenient form of hydrogen or other gas electrode and one which attains the equilibrium value very quickly, may be made as follows. A piece of round graphite rod A of any convenient size (3 mm. diameter was used) is drilled axially to within 6 mm. of the bottom. This is attached to a similar sized copper tube B, for leading in the gas, by a short length of rubber tubing C as shown in the figure. A spiral of light copper or platinum wire D, inserted as shown, ensures electrical contact between the copper and graphite. The outside surface of the graphite is then platinized in the usual manner. When gas at $^1/_4$ to $^1/_2$ of an atmosphere is forced in, it passes very slowly and uniformly through the graphite forming small bubbles over the entire surface, thus very quickly saturating the platinum black and using a minimum quantity of gas. Such an electrode supplied with hydrogen from a cylinder came to the equilibrium value[1] within $1^1/_2$ minutes and remained constant even though the electrode was in an open beaker of acid. This type of electrode is being used at this Laboratory for measurement of the reduction potential of acetylene and ethylene mixtures and is found to come to an equilibrium very much more quickly than a platinized platinum electrode and to require less gas. A glass tube can of course replace the copper tube, and the light spiral wire be carried through a seal further up the tube.



Wilke[2] tried to use a palladium tube as a hydrogen electrode in the same way as the graphite electrode described above, but found the electromotive force was dependent on both the internal and external pressures. This effect was not observed with the graphite electrode; a higher pressure only caused the electromotive force to reach equilibrium sooner. There is an essential difference between the two electrodes; the graphite is actually porous but Wilke believes the hydrogen must *diffuse* through the palladium. There is reason[3] to believe that it is monatomic hydrogen which passes through the electrode in the latter case and there may exist, therefore, on the outer surface of the palladium a slight excess of monatomic hydrogen over its equilibrium concentration. This would cause the electromotive force to be higher and to increase with increase of pressure. In the case of the graphite the diatomic hydrogen passes through and has at the surface a pressure of 1 atmosphere. The platinizing on the surface very materially stabilizes the electromotive force, and the opinion is ventured that if the palladium tube were platinized it would catalyze the formation of diatomic from the excess monatomic hydrogen and give correct values for the electromotive force dependent only on the external pressure.

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Received May 9, 1923

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[1] Measured only to 0.1 mv.

[2] Wilke, *Z. Elektrochem.*, **19**, 857 (1913).

[3] See the work of Winkelmann, *Ann. Physik*, **6**, 104 (1901).

Tetramethylammonium Tri- and Tetrachloro-iodides.—Weltzien[1] describes the preparation of the di-, tri- and tetrachloro-iodides of tetramethylammonium. No polyhalides of ammonium or the alkali metals corresponding to tetramethylammonium trichloro-iodide, $N(CH_3)_4ICl_3$, are known; it was, therefore, thought desirable to repeat Weltzien's work.

Analysis of the solid obtained by the method which Weltzien supposed to yield the trichloride gave results which were low and variable, so that the existence of this compound does not appear to be satisfactorily established; probably it is a mixture of the di- and tetrachloro-iodides produced by the partial decomposition of the latter substance.

Weltzien's analysis of the tetrachloro-iodide showed that his product was partly decomposed. A solid more closely approaching the composition of tetramethylammonium tetrachloro-iodide, $N(CH_3)_4ICl_4$, is obtained by the long continued action of dry chlorine gas on tetramethylammonium iodide at 28°. The solid was weighed in a small glass-stoppered weighing bottle, with glass inlet and outlet tubes also fitted with ground glass stoppers. A slow, continuous stream of chlorine was conveniently obtained by the electrolysis of a concd. solution of hydrochloric acid, the gas was passed through water and concd. sulfuric acid and then into the bottle containing the iodide; the latter first turned brown, then black and finally was completely converted into an orange-colored solid. The bottle was weighed from time to time with the following results:

Expt. 1. 0.5173 g. of iodide used		Expt. 2. 0.6030 g. of iodide used	
Time: days	Gain: G.	Time: days	Gain: G.
2	0.0898	38	0.3522
14	0.1874	51	0.3779
29	0.2739	77	0.3820
52 (constant)	0.3616	99 (constant)	0.4244
Total gain 69.9%		70.4%	

The formation of $N(CH_3)_4ICl_4$ requires a gain of 70.6% in weight The substance formed in Expt. 1 was analyzed; 0.8484 g. required 140.48 cc. of 0.0694 *N* arsenite equivalent to 0.3457 g. of chlorine or a gain in weight of 68.8 %.

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Received December 14, 1922

Some Solidification Curves of Binary Systems.—In a series of papers on the solidification points of binary systems of various nitro derivatives of toluenes by Professor Bell,[1] I am erroneously attributed with having in my prior researches[2] taken as the temperature of solidification of binary

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[1] Weltzien, *Ann.*, 99, 1 (1856).

[1] Bell, *J. Ind. Eng. Chem.*, **11**, 1124 (1919).

[2] Giua, *Ber.*, **47**, 1718 (1914). *Gazz. chim. ital.*, **45**, 339 (1915).

mixtures the minimum obtained as the effect of supercooling. Since this opinion is repeated by C. A. Taylor and W. H. Rinkenbach,[3] in order that the American reader may not gain the impression that I am ignorant of the most elementary rules for the determination of the point of solidification (though my book, "Chemical Combinations between the Metals," should be sufficient to demonstrate the contrary) I have replied to Professor Bell in the *Gazzetta chimica Italiana*[4] and to Messrs. Taylor and Rinkenbach in the *Giornale di chimica industriale ed applicata.*[5]

I have to state that in the solidification curve, Fig. 1, as described by Professor Bell, I have taken the point *C* and not the point *B* as the temperature of solidification. The discrepancy between my results and those of Professor Bell are due to his having taken the point *C′* as the solidification point. While my results are *experimental,* Professor Bell's are *extrapolated.* That my results are correct can be deduced also from the excellent investigation of A. L. Macleod, M. C. Pfund and M. L. Kil-

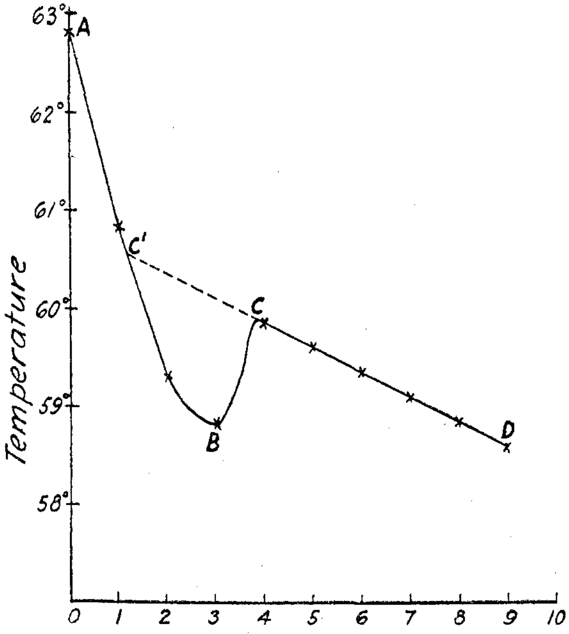

Fig. 1

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[3] Taylor and Rinkenbach, THIS JOURNAL, **45,** 44 (1923). *Ind. Eng. Chem.,* **15,** 73 (1923).

[4] Vol. II, p. 101, 1923.

[5] February, 1923.

patrick[6] who refer directly to my researches and demonstrate that Professor Bell's correction is unnecessary.

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Received March 26, 1923

In the preceding note Professor Giua states that in his experimental data he has taken the point C of the diagram as representing the freezing point of a binary mixture. In his Italian and German articles to which reference has been made he labels the recorded temperatures as "beginning of crystallization." The beginning of crystallization obviously comes at the point B, and the rise in temperature from B to C is a result of crystallization which has followed supercooling. The confusion which has arisen comes, therefore, from the misnaming of temperatures which should have been called "maximum temperatures after crystallization" and not "temperatures of the beginning of crystallization."

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Received April 21, 1923

An Intercepted Hydrolysis.—In one of a series of experiments designed to bring about the formation of phosphonium cyanide, potassium cyanide was heated with stick phosphorus and a little water, in an atmosphere of hydrogen. The free caustic potash in the solution of potassium cyanide was expected to react with the phosphorus to give phosphine, the corresponding amount of liberated hydrogen cyanide providing an opportunity for combination. The gases evolved were passed over warm phosphorus pentoxide, and a white, crystalline product was collected in a cooled receiver. On analysis, this substance proved to be a very pure sample of ammonium cyanide, containing no phosphorus whatever.

The history of the reaction must be as follows. At ordinary temperatures, in a closed vessel, we have the equilibrium, $KCN + H_2O \rightleftharpoons KOH + HCN$. At higher temperatures, this equilibrium is destroyed by the disappearance, through further hydrolysis, of the hydrogen cyanide, $HCN + 2H_2O = NH_4OOCH$, which is a *complete* action, the ammonium formate being destroyed by the equivalent potassium hydroxide formed: $KOH + NH_4OOCH = NH_3 + HCOOK + H_2O$. In sum, $KCN + 2H_2O = NH_3 + HCOOK$, and when potassium cyanide is boiled with water, nearly all of the gas evolved is ammonia.

When phosphorus is present the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide

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[6] Macleod, Pfund and Kilpatrick, THIS JOURNAL, **44**, 2260 (1922).

present, an equivalent amount of hydrogen cyanide being liberated. With a large excess of water, we should probably have $3KCN + 4P + 12H_2O = 3KH_2PO_2 + PH_3 + 3HCOONH_4$, but this excess is not present, and after a small amount of ammonium formate has formed, we reach equilibrium and hydrogen cyanide is liberally evolved.

There is, thus, a main reaction, $KCN + 2H_2O = NH_3 + HCOOK$, and a subsidiary reaction, $3KCN + 4P + 6H_2O = 3KH_2PO_2 + PH_3 + 3HCN$. We refer to them in this manner because the ammonia evolved was always in excess over the hydrogen cyanide.

The experiment was repeated with other non-volatile substances, reactive with potassium hydroxide. Aluminum powder, in place of phosphorus, also produced ammonium cyanide of great purity. A greatly superior yield, however, was obtained by using a suitable proportion of sulfuric acid. Attention was called in this case to the great readiness with which ammonium cyanide is oxidized. In the first trials of the sulfuric acid method, hydrogen was neither formed in the reaction (as in the case of aluminum) nor flushed through the apparatus (as in the case of phosphorus). The product was ochreous in appearance, and was sublimed only with difficulty. The cause of this proved to be the formation of a matrix of azulmic acid, produced, we think, as follows.

$$2NH_4CN + O = 2NH_3 + C_2N_2 + H_2O. \quad NH_4CN \rightleftharpoons NH_3 + HCN$$

$$2NH_3 + 2C_2N_2 = C_4H_6N_6 \text{ (Hydrazulmin)}. \quad C_4H_6N_6 + H_2O = C_4H_5N_5O + NH_3.$$

It has often been remarked that while ammonia is effectively administered in cases of prussic acid poisoning, ammonium cyanide is powerfully poisonous. As, however, this substance cannot exist at the temperature of the body, its effects are probably due to the formation of cyanogen, as shown above, through a damp oxidation. Ammonium cyanide is most readily ignited, burning with a pale, fawn-colored flame. It immediately decolorizes neutral potassium permanganate solution: when the latter is added drop by drop until the decolorization is *slow*, a vivid yellow solution is formed, and this does not become brown nor deposit hydroxides until after standing exposed to the air for many hours.

Similarly, ammonium cyanide is reactive with sulfur. When it is dissolved in a chloroform solution of sulfur, thin leaves of ammonium thiocyanate separate on partial evaporation.

CONTRIBUTION FROM THE
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