not pyrophoric and did not regain their black color or pyrophoric property by allowing them to cool in an atmosphere of hydrogen.

Summary

Nickel salts are reduced by sodium, potassium or calcium to free nickel. It is pyrophoric and an excellent catalyst for the reaction between sodium (potassium or calcium) and ammonia. Small amounts of nickel amide are formed when the nickel salt is present in excess. The reactivity of the nickel is greater when calcium is the reducing metal. The pyrophoric property appears to be due to adsorbed hydrogen.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Transference Numbers of Sulfuric Acid in Anhydrous Methanol at 25°[1]

BY E. W. KANNING AND J. E. WALTZ

Transference numbers of sulfuric acid in aqueous solutions have been estimated[2] from a combination of the data of the electromotive force of cells without liquid junctions and of concentration cells with transference. Measurements are reported for the cells

$$\mathrm{Pt(H_2)} \mid \mathrm{H_2SO_4} \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg} \qquad \text{(I)}$$

and

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{H_2SO_4}(m_1) \parallel \mathrm{H_2SO_4}(m_2) \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg} \qquad \text{(II)}$$

Activity coefficients have been calculated from data obtained with Cell I. Moreover, the difference of various combinations of Cell I may be represented as the electromotive force of concentration cells without transference.[3] The relation is expressed in differential form as

$$\mathrm{d}E = (-3RT/2F)\mathrm{d}(\ln a)$$

where a is the geometric mean activity of the ions. The differential expression for the potential of Cell II is given as

$$\mathrm{d}E_t = (-3RT/2F)t_{\mathrm{H}^+}\ \mathrm{d}(\ln a)$$

where t_{H^+} is the transference number of the ions to which the electrodes are not reversible. If $\mathrm{d}E$ and $\mathrm{d}E_t$ were plotted as the ordinates against $\mathrm{d}(\ln a)$ as abscissa, the transference number, t_{H^+}, can be estimated by computing the ratio of the slopes of the two curves.

The purpose of this investigation was to study the applicability of this method for the determination of transference numbers of sulfuric acid in other than aqueous solutions. Some preliminary studies are here reported on solutions in anhydrous methanol.

Experimental

Materials.—About 5 g. of sodium hydroxide and 15 g. of iodine were added to each liter of methanol to be purified; the mixture was allowed to stand for twenty-four hours. The solution was then refluxed for six hours and distilled. After this treatment the methanol showed a negative test for aldehydes and ketones when warmed with an equal volume of 6 *N* sodium hydroxide solution saturated with mercuric cyanide. The water was removed by the method of Lund and Bjerrum.[4] Basic impurities were removed by a final distillation from sulfanilic acid. The sulfuric acid used (m. p. 10.4°) was prepared by the method of Kendall and Carpenter.[5] The mercury–mercurous sulfate electrodes were made from twice distilled C. P. mercury and electrolytically prepared mercurous sulfate.[6] The hydrogen electrodes were platinized and treated according to the directions of Popoff, Kunz and Snow.[7]

Procedure.—Measurements of the potentials of Cells I and II were made with a Leeds and Northrup type K-2 potentiometer, a type R galvanometer, and an Eppley standard cell which was certified by its manufacturer and checked frequently with another certified cell. Cell I was of the H-type with two electrodes in each half-cell. The stoppers were fitted with stopcocks and interchangeable ground glass joints in order that the cell could be flushed with hydrogen and filled without the solution coming into contact with air. Purified tank hydrogen was used. A saturating bottle containing the cell solution was interposed between the purification train and the cell. In the concentration range for which measurements are reported, the potentials of this cell were constant and reproducible to about 0.1 mv. Cell II, with some modifications, was essentially the same as that described by MacInnes and Beattie.[8] The junction was formed in the center of a 34/45 Pyrex ground glass joint through 12-mm. tubing drawn to 4 mm. at the junction, with the tips about 5 mm. apart.

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[1] This paper is constructed from a dissertation presented by Joseph Elmer Waltz to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Harned and Hamer, THIS JOURNAL, **57**, 27 (1935); Hamer, *ibid.*, **57**, 662 (1935).

[3] D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, pp. 168–169.

[4] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[5] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[6] See Carhart and Hulet, *Trans. Am. Electrochem. Soc.*, **5**, 59 (1904).

[7] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

[8] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).

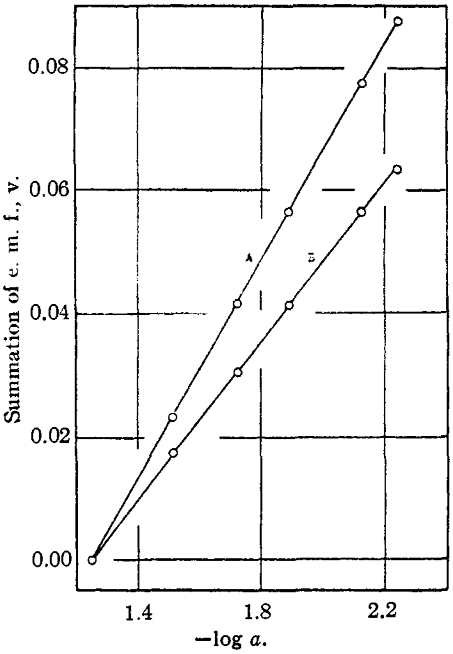

Fig. 2.—Plot of the summation of the potentials of Cells I and II against $-\log a$.

e. m. f. of the cell concentrations 0.27714 and 0.07151 is added to the e. m. f. of the cell of concentrations 0.54434 and 0.27714, etc.) Curve A is a straight line having the theoretical slope $3RT/2F$. The slope of Curve B was determined by differentiating a cubic equation fitted analytically to the four best points of the curve. The empirical equation obtained was

$$E_t = -0.08641 + 0.07336(-\log a) - 0.00425(-\log^2 a) + 0.00067(-\log^3 a)$$

This equation was differentiated with respect to $-\log a$, and the constants were divided by the slope of line A (0.08868), with the result

$$t_{H^-} = 0.827 - 0\ 0958(-\log a) + 0.0226(-\log^2 a)$$

The cation transference numbers computed by this method[8] are

m	0.54434	0.27714	0.14118	0.07151	0.02522	0.01375
t_{H^+}	0.742	0.734	0.729	0.727	0.725	0.726

The transference numbers increase with increasing concentrations and are smaller by about 0.1 than those reported by Hamer[2] for aqueous solutions of sulfuric acid. This may be expected, since solvation of the proton by the heavier methanol molecule should diminish mobility with respect to the sulfate ion to a greater extent than in aqueous solutions.

It is recognized that the method described above does not have the precision of the modern moving-boundary methods, but it does yield at least a reasonably accurate approximation of transference numbers in solutions where no data of the kind are available. The error possibly introduced by a questionable assignment of activity coefficients is not great, since in Fig. 2 any constant times the activity could have been plotted. The principal limitation of the accuracy lies in the readings of the potential of the concentration cell, since a difference of potential of 0.02 mv. represents a change of 0.001 in the transference number. This difficulty is particularly significant in dilute solutions, where the solubility of mercurous sulfate in methanol is sufficient to be troublesome.

Summary

The activity coefficients and cation transference numbers of sulfuric acid in anhydrous methanol were determined at 25° by the e. m. f. method over a concentration range of 0.5443 *m* to 0.01375 *m*.

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