

Fig. 1.—The solubility of barium nitrate in nitric acid: O, experiments at 24.88°; ●, experiments at 0.00°; +, experiments of Tolmachev.⁸

From 55 to 80% of nitric acid the logarithms of the solubilities fall upon a smooth curve which may be expressed well by a quadratic function of the per cent. of nitric acid. Coefficients for this

function were determined by the method of least squares omitting the points above 80% of acid because of the obvious experimental uncertainties in this range. The resulting equations have been used to compute the values in column 6 of Table I and the solubilities at round concentrations of nitric acid in Table II.

At 24.88° the solubility is given by the equation

$$\log(\% \text{Ba}(\text{NO}_3)_2) = 0.24537 - 0.0006232 (\% \text{HNO}_3) - 0.0006351 (\% \text{HNO}_3)^2 \quad (1)$$

while at 0.00° the equation is

$$\log(\% \text{Ba}(\text{NO}_3)_2) = -0.53778 + 0.0189055 (\% \text{HNO}_3) - 0.00079706 (\% \text{HNO}_3)^2 \quad (2)$$

These equations represent well the results of the present experiments in the concentration range from 50 to 90% nitric acid. As is shown by the dashed curve in Fig. 1 they are entirely unreliable in dilute nitric acid. The extrapolation to 100% HNO₃ in Table II is interesting but uncertain.

TABLE II

THE SOLUBILITY OF BARIUM NITRATE IN NITRIC ACID
CALCULATED BY EQUATIONS (1) AND (2)

HNO ₃ , %	% Ba(NO ₃) ₂ 24.88°C.	% Ba(NO ₃) ₂ 0.00°C.
50	0.0423	0.0260
60	.00835	.00533
70	.00123	.000759
80	.000135	.0000747
90	.0000111	(.00000509)
100	(.00000068)	(.00000024)

Summary

The solubility of barium nitrate has been measured at 0.00 and 24.88° in concentrations of nitric acid ranging up to 92%. Equations have been derived which express the logarithm of the solubility as a quadratic function of the per cent. of acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Normal Potential of the Mercury–Mercurous Iodide Electrode at 25°¹

BY ROGER G. BATES AND WARREN C. VOSBURGH

For the normal potential of the mercury–mercurous iodide electrode, the value of 0.0416 v. at 25° is given by "International Critical Tables."² This value was calculated from the electromotive force of the lead–mercurous iodide cell measured by Vosburgh³ and a value for the normal potential of the lead amalgam–lead iodide electrode. However, values for the latter electrode calculated from data for different cells⁴ do not agree well. In

view of the resulting uncertainty, it was decided to determine the normal potential of the mercurous iodide electrode directly, since its value was needed in another investigation.

Materials.—Mercury was purified by washing with an acidified mercurous nitrate solution and distilling twice at reduced pressure in a current of air. Mercurous iodide was prepared by precipitation and digestion as described by Vosburgh³ for his Preparation 7. Potassium iodide was recrystallized twice from redistilled water and dried for about a week at 110–125°. Analysis by the Volhard method indicated a purity of at least 99.9%. Hydrogen was prepared by the electrolysis of 30% sodium hydroxide solution and was passed through a tube containing a hot platinum wire for removal of oxygen.

Preparation and Measurement of the Cells.—Two series of cells were made, one with electrolytes of potassium

(1) Part of a thesis submitted by Roger G. Bates in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) "International Critical Tables," Vol. VI, p. 332.

(3) Vosburgh, *THIS JOURNAL*, **50**, 2391 (1928).

(4) (a) Gerke, *ibid.*, **44**, 1701–1703 (1922); (b) Getman, *J. Phys. Chem.*, **32**, 944 (1928); (c) Jones and Kaplan, *THIS JOURNAL*, **50**, 2076 (1928); (d) Owen, *ibid.*, **57**, 1526 (1935).

iodide and hydrochloric acid and the other with electrolytes of potassium iodide, acetic acid and sodium acetate. Solutions of potassium iodide and borax^{4d} were tried with poor results, probably because the solutions were too alkaline for the stable existence of mercurous iodide. Care was taken to keep the solutions free from oxygen by the use of purified nitrogen. The cell vessels were of the type shown in Fig. 1 and were of Pyrex glass. The sealed-in contact for the mercurous iodide electrode was of tungsten wire. Platinum black electrodes were prepared essentially as described by Popoff, Kunz and Snow.⁵

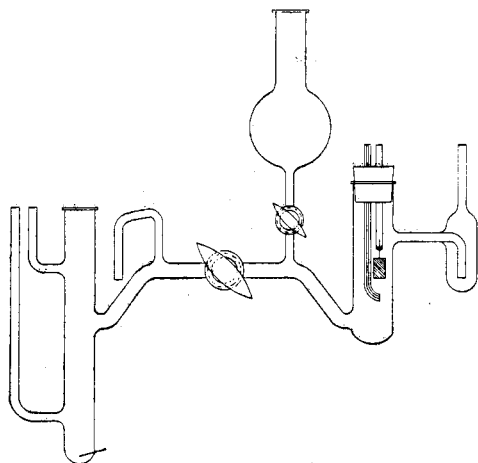


Fig. 1.

The solutions of hydrochloric acid and potassium iodide were prepared by weight from redistilled water, the purified potassium iodide and constant-boiling hydrochloric acid solution of known composition. In preparing the mercurous iodide electrodes, oxygen was removed from around the mercury by evacuation and special care was taken to wash the mercurous iodide thoroughly by vigorous mechanical stirring with the electrolyte. The last washing was made with oxygen-free electrolyte. After introduction into the cell vessel, in which the air had been replaced by nitrogen, the solution above the mercurous iodide layer was replaced three times with oxygen-free electrolyte. The mercurous iodide electrodes were made at least ten hours before the hydrogen electrodes, to give time for the attainment of equilibrium. In the preparation of the hydrogen electrodes and the measurement of the electromotive forces, special care was taken to prevent the entrance of mercurous ion.

After preparation, the cells were brought to constant temperature in an air-bath at 25° in which fluctuations as measured by a thermometer were of the order of ±0.05°. The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer, using as reference standards a set of five non-portable, saturated Weston cells that had been recently checked by the Bureau of Standards. The results are given in Table I. Each electromotive force is the mean for two cells agreeing on the average within 0.08 mv. and in all cases within 0.23 mv., and of satisfactory constancy. The electromotive forces given in the table have been corrected to a hydrogen

partial pressure of one atmosphere. The compositions of the electrolytes are given in millimoles per 1000 g. of water ($m \times 10^3$) and μ is the ionic strength.

TABLE I

THE CELL: $H_2(Pt)/HCl, KI/HCl, KI, Hg_2I_2/Hg$

HCl, $m \times 10^3$	KI, $m \times 10^3$	μ	E_{25} corr., v.	$E_{25}^{0'}$, v.
12.45	10.47	0.0229	0.19631	-0.04074
16.31	12.38	.0287	.18572	-.04064
19.52	9.90	.0294	.18669	-.04088
27.72	10.15	.0379	.17781	-.04088
25.91	19.68	.0456	.16300	-.04102
40.64	14.88	.0555	.15913	-.04112
65.61	10.07	.0757	.15775	-.04107
91.80	10.60	.1024	.14865	-.04131

The values for $E_{25}^{0'}$ in the last column of Table I were calculated from the values of E_{25} by the equation

$$E_{25}^{0'} = E_{25} - k \log [HCl][KI] \gamma^2$$

in which brackets indicate molalities and $k = 2.303 RT/F$ and the activity coefficient, γ , was the activity coefficient for hydrochloric acid at the ionic strength in question. Curve I of Fig. 2 is a plot of $E_{25}^{0'}$ against ionic strength.

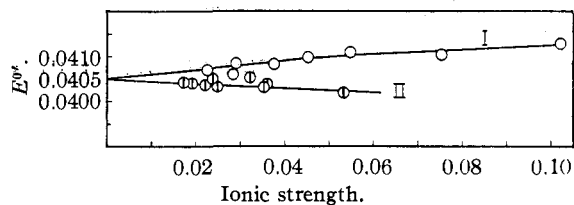


Fig. 2.—Variation of $E_{25}^{0'}$ with ionic strength. Curve I represents cells with electrolytes of hydrochloric acid and potassium iodide and Curve II cells with electrolytes of acetic acid, sodium acetate and potassium iodide.

For the second series of cells, solutions of acetic acid and carbonate-free sodium hydroxide of nearly equal concentrations were carefully standardized, using potassium acid phthalate as the primary standard. To make the cell electrolytes these solutions were mixed in the proportion of two volumes of the acid solution to one of the alkali and diluted by weight to the desired molality.

TABLE II

THE CELL: $H_2(Pt)/HOAc, NaOAc, KI/HOAc, NaOAc, KI, Hg_2I_2/Hg$

HOAc, $m \times 10^3$	NaOAc, $m \times 10^3$	ρ	KI, $m \times 10^3$	μ	E_{25} (corr.), v.	$E_{25}^{0'}$, v.
10.24	10.24	0.9966	7.388	0.0176	0.36712	-0.04047
9.638	9.638	.9964	9.745	.0194	.36003	-.04044
13.17	12.14	1.082	10.27	.0224	.35660	-.04042
13.93	13.93	0.9975	10.05	.0240	.35912	-.04054
14.91	14.91	.9976	10.17	.0251	.35900	-.04037
19.09	17.60	1.083	14.88	.0325	.34890	-.04057
22.79	21.01	1.083	14.64	.0357	.34752	-.04086
23.38	23.38	0.9985	12.79	.0362	.35303	-.04041
34.70	34.70	.9990	18.98	.0537	.34306	-.04023

(5) Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

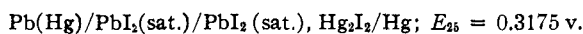
Oxygen was removed by a current of nitrogen, and a known weight of potassium iodide was added. The data for the cells made with these solutions are given in Table II. The reproducibility was better than for the first series; differences between duplicates were not larger than 0.09 mv., and the average was 0.03 mv.

The quantity ρ in Table II is the ratio of the molality of un-ionized acetic acid to the molality of acetate ion. The values for $E_{25}^{0'}$ were calculated by the equation^{4d}

$$E_{25}^{0'} = E_{25}^0 - f(\gamma) = E_{25}^0 + k \log [KI] + k \log \rho + k \log K_{\text{HOAc}}$$

in which K_{HOAc} is the ionization constant of acetic acid for which the value 1.754×10^{-5} was used.⁶ The value of $f(\gamma)$ is small and should become zero when $\mu = 0$. The relation of $E_{25}^{0'}$ to ionic strength is shown by Curve II of Fig. 2. Extrapolation to infinite dilution gives a value for E_{25}^0 in good agreement with the value from the first series of cells, and $E_{25}^0 = -0.0405$ v. can be taken as the best value.

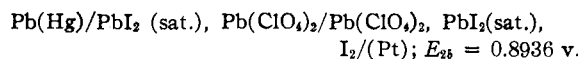
Discussion. Combining $E_{25}^0 = -0.0405$ v. with the electromotive force of the cell⁸



- (6) (a) Harned and Ehlers, *THIS JOURNAL*, **54**, 1356 (1932);
 (b) MacInnes and Shedlovsky, *ibid.*, **54**, 1438 (1932).

gives for the lead amalgam-lead iodide electrode the normal potential $E_{25}^0 = 0.3580$. For this electrode Gerke⁷ calculated 0.3579 v. while "International Critical Tables"² gives 0.3591 v.

Combination of the value $E_{25}^0 = 0.3580$ v. with the electromotive force of the cell^{4a}



gives $E_{25}^0 = -0.5356$ v. for the normal potential of the iodine electrode. Jones and Kaplan^{4c} found -0.5362 v., "International Critical Tables"² gives -0.5345 v. and Lewis and Randall⁸ give -0.5357 v.

Summary

Measurements were made at 25° of the electromotive force of the cell Hg/Hg₂I₂, HI/HI/H₂(Pt), in which the hydriodic acid was furnished either by a solution of potassium iodide and hydrochloric acid or by a solution of potassium iodide, acetic acid and sodium acetate. The value of E_{25}^0 was found to be 0.0405 v. From this value and data from the literature, normal potentials for the lead amalgam-lead iodide and iodine electrodes were calculated.

(7) Gerke, *Chem. Reviews*, **1**, 377 (1925).

(8) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923, p. 430.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

A Study of the Precipitation of Aluminum Basic Sulfate by Urea¹

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In the separation of metals by precipitation as hydroxides, hydrous oxides or basic salts, the necessity for a careful control of pH is obvious. Sufficient attention has, however, not been given to the advantage of keeping the solution homogeneous with respect to pH. If the pH becomes too high locally, as, for example, by the addition of a base, even a weak one, the precipitation of some other hydroxide is facilitated, and if this occurs it may not dissolve when the solution is thoroughly mixed. Yet this is the usual method of precipitation. The best method of accomplishing this result is by the use of a substance which, dissolved

in the solution, will slowly decompose so as to bring about neutralization of the acid. The following types of reagents have been used in an attempt to maintain the proper pH: buffers, such as acetic acid and acetate; insoluble oxides and carbonates, such as zinc oxide; weak bases, mostly organic, such as phenylhydrazine and pyridine; compounds which decompose with liberation of ammonia, such as hexamethylenetetramine and potassium cyanate; substances which decompose in hot solution with the formation of a volatile acidic constituent, such as sodium thiosulfate and ammonium nitrite; mixtures of halides, halates and halogen acids, such as iodate and iodide, bromate and bromide, bromate and chloride.³

(1) Original manuscript received January 30, 1934.

(2) Rockefeller Foundation Fellow. From a dissertation presented by N. K. Tang in 1930 to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) For the sake of brevity a review of the literature has been omitted, but is given in the dissertation.