JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (Copyright, 1951, by the American Chemical Society)

VOLUME 73 FEBRUARY 15, 1951 NUMBER 2

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY AND THE UNIVERSITY OF OREGON]

The Equilibria of Two Basic Bismuth Nitrates in Dilute Nitric Acid at 25°[1]

BY D. F. SWINEHART[2] AND A. B. GARRETT

The solubilities of two basic bismuth nitrates, $BiONO_3$ and $BiO(OH)BiONO_3$, in nitric acid in the concentration range 0.005 to 0.2 molal have been measured. The "triple point" where the two solid phases are in equilibrium with the saturated solution occurs at $m_{H^+} = 0.065$ and $m_{Bi} = 1.50 \times 10^{-3}$. By calculation of equilibrium constants it is shown that the reaction $BiONO_3(s) + 2H^+ = Bi^{+++} + NO_3^- + H_2O$ accounts completely for the solubility of bismuthyl nitrate in dilute nitric acid. The equilibrium constant for this reaction is 2.8×10^{-3}. The ion $Bi(OH)^{++}$ is not formed in appreciable quantities.

A study of bismuth oxide in dilute acidic and basic solutions[3] indicated that bismuth oxide is converted to a white basic salt when it is equilibrated with dilute solutions of nitric acid. Two such salts have been identified; they are bismuthyl nitrate, $BiONO_3$, and a more basic nitrate, $BiO(OH)BiONO_3$. In this paper are presented data on the solubility of these two salts in dilute solutions of nitric acid. Data in a higher concentration range have been obtained for bismuthyl nitrate by Smith.[4]

Experimental

The general procedure was the same as that of Garrett and Heiks[5] in their study of stannous hydroxide.

Water of a conductivity less than 1×10^{-6} mho was used in the preparation of all solutions. All preparations and equilibria were made or obtained in an atmosphere of nitrogen.

Grasselli C.P. Nitric Acid and Baker and Adamson Reagent Bismuth Trinitrate Pentahydrate were used without further purification. Carbonate-free sodium hydroxide was prepared by adding a slight excess of barium oxide to a solution of sodium hydroxide.

Bismuth oxide, Bi_2O_3, was prepared from bismuth hydroxide which was precipitated in an atmosphere of purified nitrogen by the dropwise mixing of 1.5 molar carbonate-free sodium hydroxide and 0.1 molar bismuth nitrate in 1.0 molar nitric acid at 80–90°. The solution was kept alkaline during the entire precipitation. The newly formed precipitate was white and flocculent but, on being agitated for a short time in the hot solution, it dehydrated to the light yellow oxide. The oxide was washed 15 times by decantation with air-free, carbon dioxide-free water. This product was found to contain a small amount of silica but, since the oxide was always converted to a basic nitrate on contact with nitric acid, this impurity was assumed to have no effect upon the equilibria reported in this study.

Bismuthyl nitrate, $BiONO_3$, was prepared by diluting a solution of 60 g. of $Bi(NO_3)_3 \cdot 5H_2O$ (in as little 6 molar nitric acid as possible) with water until precipitation was nearly complete. The precipitate was washed repeatedly with dilute (*ca.* 0.02–0.05 *m*) nitric acid. The product consisted of white shiny platelets and was kept wet in the preparation of samples for equilibration. Small samples which were dried at 110° and analyzed by ignition to the oxide gave an average analysis of 80.9 ± 0.1% Bi_2O_3 (theoretical for $BiONO_3$, 81.2% Bi_2O_3). The samples could not be washed thoroughly with water because of the danger of further hydrolysis. Attempts to dry the samples at room temperature did not prove conclusively that the product was the monohydrate so the formula $BiONO_3$ will be used here.

Samples for equilibration were prepared by introducing excess bismuth oxide or bismuthyl nitrate into nitrogen filled 200-ml. Pyrex flasks, filling with the appropriate acid solution and sealing off the neck with an oxyhydrogen flame to avoid introduction of carbon dioxide.

Samples were made up in pairs and equilibrium was approached from undersaturation and supersaturation by agitating one of the pair at approximately 40° for 3–5 days before placing it in the 25 ±0.05° bath along with its mate. The equilibrium period was 2 to 3 weeks.

The samples were sedimented at 25° until free of a Tyndall beam, opened and filtered through a sintered glass disc under nitrogen pressure.

Measurements of *p*H were made with a Coleman vacuum tube *p*H meter. The instrument was calibrated against standard nitric acid solutions. The activity of hydrogen ion was calculated in each case from the concentration and the activity coefficient of hydrogen ion, the latter being taken equal to the mean activity coefficient of nitric acid as indicated by the Debye–Hückel limiting law. The mean activity coefficients of nitric acid were taken from the data of Hartman and Rosenfeld.[6] In measuring the *p*H of the equilibrated samples, the liquid junction was flushed before each determination and repeated small samples of the freshly filtered solution were measured until a constant value was

---

[1] Presented at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington, May 3, 1947.

[2] University of Oregon, Eugene, Oregon.

[3] Unpublished.

[4] D. F. Smith, THIS JOURNAL, **45**, 360 (1923).

[5] Garrett and Heiks, *ibid.*, **63**, 562 (1941).

[6] Hartman and Rosenfeld, *Z. physik. Chem.*, **A164**, 377 (1933).

obtained. *p*H values were reproducible to ±0.02 *p*H unit.

Bismuth analyses were carried out polarographically by the method of Swinehart, Garrett and MacNevin.[7]

The Data

The data are shown in Table I and Fig. 1. Rounded data[8] are shown in Table II.

Table I

Solubility of $BiO(OH)BiONO_3$ in HNO_3 Solutions; Initial Solid Phase, Bi_2O_3

a_H (glass electrode)	Concn. of Bi (gram atoms per 1000 g. H_2O)^a	a_H (glass electrode)	Concn. of Bi (gram atoms per 1000 g. H_2O)^a
0.0042	$1.45^u \times 10^{-5}$	0.040	26.4^s
.0064	1.86^s	.046	31.5^s
.014	3.88^s	.049	33.8^s
.020	5.85^s	.049	73.9^s
.022	7.16	.051	45.4^s
.028	14.0	.051	65.1^s
.035	14.3^s	.051	82.9^s
.038	23.3		

[a], [u] undersaturation value only. [s] supersaturation value only.

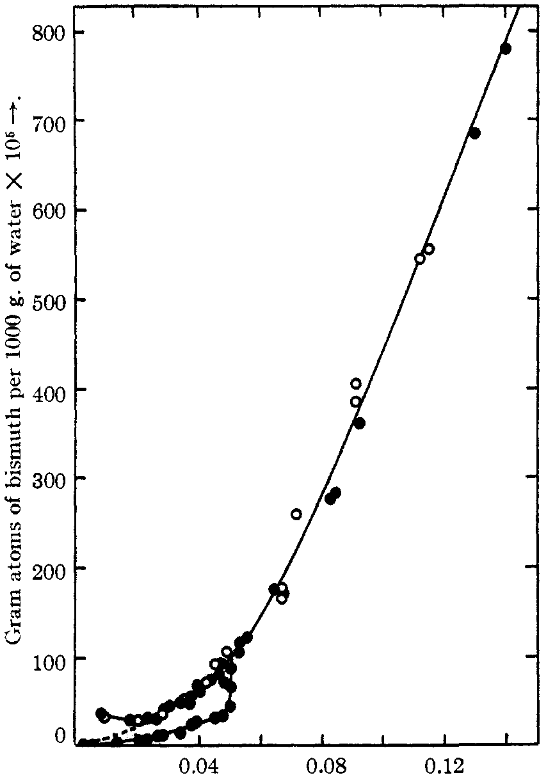

Fig. 1.—Solubility of two basic bismuth nitrates in nitric acid: upper curve, $BiONO_3$; lower curve, $BiO(OH)BiONO_3$. O, initial solid phase, $BiONO_3$; ●, initial solid phase, Bi_2O_3.

All of the data were obtained by using bismuth oxide or bismuthyl nitrate as the initial solid phases. In all cases bismuth oxide was converted to a basic salt either of the formula $BiONO_3$ or $BiO(OH)BiONO_3$. In all samples sufficient nitric acid was added to convert completely all of the oxide to the basic salt. The equilibria involved in this study are those in which one or the other of these basic salts are the solid phases. The solubility of these two solid phases in nitric acid are shown by the two curves in Fig. 1. In the case of bismuthyl nitrate the data indicate that the same equilibrium results are obtained from either bismuth oxide or bismuthyl nitrate as the initial solid phase.

The identity of the solid phase was determined in each case. The solid phase from the samples which fell on the lower curve, on being analyzed by ignition to the oxide, gave an average value of 87.5 ± 0.2% Bi_2O_3. This corresponds to the formula $BiO(OH)BiONO_3$ (theoretical for $BiO(OH)BiONO_3$—88.1% Bi_2O_3). The solid phases from the samples which fell on the upper curve showed an average of 81.5 ± 0.5% Bi_2O_3 corresponding to $BiONO_3$ (theoretical for $BiONO_3$—81.2% Bi_2O_3). The variation in the analyses was due, at least in part, to the impossibility of washing the samples. The solutions were simply decanted, the solid drained, dried at 110° and ignited to the oxide.

When the initial solid phase was Bi_2O_3 it frequently happened, although not always, that the member of a pair which approached equilibrium from supersaturation by stirring at about 40° before the final equilibration at 25° fell on the lower curve, thus showing the greater hydrolysis, while its partner fell on the upper curve. Thus most of the solubility values for the lower curve (Table I) were obtained from supersaturation only.

The "triple point" where both $BiONO_3$ and $BiO(OH)BiONO_3$ are in equilibrium with the saturated solution occurs at an activity of hydrogen ion of 0.052 (a molality of 0.065) and a molality of bismuth of 1.05×10^{-3}.

Discussion

The $BiONO_3$-HNO_3 Equilibrium.—It is assumed that the solubility of $BiONO_3$ in dilute nitric acid solutions can be accounted for by one or more of the reactions

$$BiONO_3(s) = BiONO_3(aq) \quad (1)$$
$$BiONO_3(s) = BiO^+ + NO_3^- \quad (2)$$
$$BiONO_3(s) + H^+ = Bi(OH)^{++} + NO_3^- \quad (3)$$
$$BiONO_3(s) + 2H^+ = Bi^{+++} + NO_3^- + H_2O \quad (4)$$

Figure 1 indicates that both curves extrapolate into the origin, so no appreciable contributions to the solubility are made by the reactions indicated by equations (1) and (2), at least at activities of hydrogen ion above 0.02, within the limits of experimental error. Below a_{H^+} = 0.02 the upper curve appears to be turning upward and, if no further hydrolysis occurred, presumably it would rise to a value corresponding to the water solubility of $BiONO_3$ and show the common ion effect of the depression of the solubility by nitric acid.

For equation (3) the equilibrium constant is

$$K_3 = (m_{Bi(OH)^{++}} m_{NO_3^-} \gamma_{Bi(OH)^{++}} \gamma_{NO_3^-})/(m_{H^+} \gamma_{H^+})$$

Multiplying numerator and denominator by $\gamma_{NO_3^-}$ and using the relation from the Debye–Hückel

---

(7) Swinehart, Garrett and MacNevin, *Ind. Eng. Chem., Anal. Ed.*, **15**, 729 (1943).

(8) For detailed data order Document 2927 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

TABLE II

SMOOTHED DATA FOR $BiONO_3$ IN HNO_3 SOLUTIONS

a_{H^+}	Concn. of Bi, (S), (gram atoms per 1000 g. H_2O)	m_{H^+}	γ_{HNO_3}	Ionic strength	$(S\gamma^4_{HNO_3} m_{NO_3^-})/m_{H^+}$	$m_{H^+}/\gamma^4_{HNO_3}$	K_4
0.0250	32×10^{-5}	0.0295	0.848	0.0314	17.1×10^{-5}	0.057	3.00×10^{-3}
.0300	39	.0358	.839	.0381	20.0	.072	2.76
.0350	51	.0422	.829	.0453	25.0	.089	2.79
.0400	65	.0488	.820	.0527	30.5	.108	2.83
.0450	81	.0554	.812	.0603	36.8	.128	2.89
.0500	99	.0619	.806	.0678	43.8	.146	3.00
.0600	140	.0754	.795	.0838	59.1	.189	3.14
.0700	194	.0892	.784	.101	78.4	.237	3.40
.0800	261	.103	.777	.119	103	.282	3.64
.0900	342	.117	.769	.137	130	.335	3.88
.100	430	.131	.761	.158	158	.391	4.08
.110	522	.146	.755	.177	188	.450	4.16
.120	616	.160	.749	.197	216	.510	4.24
.130	715	.175	.742	.218	244	.575	4.21
.150	920	.206	.729	.261	294	.730	4.01

limiting law that the mean activity coefficient of a 2–1 electrolyte is the square of that of a 1–1 electrolyte in solutions of the same ionic strength, we obtain

$$K_3 = (m_{Bi(OH)^{++}} m_{NO_3^-} \gamma^4_{HNO_3})/m_{H^+} \qquad (5)$$

If we were to assume that equation (3) alone accounts for the solubility, *S*, of bismuthyl nitrate in nitric acid this would become $K_3 = S\gamma^4_{HNO_3} m_{NO_3^-}/m_{H^+}$. In Table II this quantity is calculated from data taken from the smooth curve in Fig. 1. It is seen to vary 17-fold for an acid concentration range of 7-fold. Hence equation (3) alone cannot account for the increase in solubility.

If we assume that the reaction indicated by equation (4) also takes place we may write

$$K_4 = (m_{Bi^{+++}} m_{NO_3^-} a_{H_2O} \gamma_{Bi^{+++}} \gamma_{NO_3^-})/(m^2_{H^+} \gamma^2_{H^+}) \qquad (6)$$

Mutiplying numerator and denominator by $\gamma^2_{NO_3^-}$, using the Debye–Hückel limiting law and $a_{H_2O} = 1$, we have

$$K_4 = [(m_{Bi^{+++}} m_{NO_3^-})/m^2_{H^+}]\ \gamma^8_{HNO_3} \qquad (7)$$

Now *S*, the total concentration of bismuth, is given by

$$S = m_{Bi(OH)^{++}} + m_{Bi^{+++}} \qquad (8)$$

Eliminating $m_{(Bi)OH^{++}}$ and $m_{Bi^{+++}}$ from equations, (5), (7) and (8) yields

$$S\gamma^4_{HNO_3} m_{NO_3^-}/m_{H^+} = K_3 + K_4\ m_{H^+}/\gamma^4_{HNO_3}$$

This predicts a straight line for a plot of $S\gamma^4_{HNO_3}$ $m_{NO_3^-}/m_{H^+}$ vs. $m_{H^+}/\gamma^4_{HNO_3}$ with K_3 as intercept and K_4 as slope. These quantities calculated from data from the smooth curve in Fig. 1 are shown in Table II and are plotted in Fig. 2. The plot shows curvature but it extrapolates into the origin with a limiting slope at $m_{H^+} = 0$ of 2.6×10^{-3}. Thus K_3 is small compared to K_4, *i. e.*, $Bi(OH)^{++}$ is not formed in appreciable quantities, and $K_4 = 2.6 \times 10^{-3}$. The deviation of this curve from linearity is probably due to the failure of the Debye–Hückel limiting law to hold for high valence ions at these values of the ionic strength.

In Table II the value of $m_{NO_3^-}$ was calculated from the equation $m_{NO_3^-} = m_{H^+} + 3S$. The term 3*S* is much smaller than m_{H^+} and $m_{NO_3^-}/m_{H^+}$ is not far from unity throughout the concentration range studied in this research. The use of the factor 3 is justified by the final conclusion that equation (4) accounts completely for the increase in solubility of bismuthyl nitrate in nitric acid solutions. The same final result would have been obtained if 2*S* had been used instead of 3*S*.

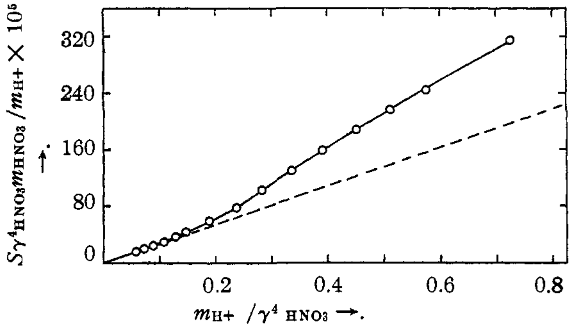

Fig. 2.—Evaluation of equilibrium constants K_3 and K_4.

K_4 may be evaluated by two other methods, each of which involves calculating values of K_4 directly (assuming $S = m_{Bi^{+++}}$), plotting the values against m_{H^+}, and extrapolating to $m_{H^+} = 0$.

The first of these methods uses equation (7) directly. These values of K_4 are shown in the eighth column of Table II and are observed to vary from 2.8 to 4.2×10^{-3}. A plot of these values *vs.* m_{H^+} was extrapolated to $m_{H^+} = 0$ yielding $K_4 = 2.6 \times 10^{-3}$.

The second of these methods of calculating K_4 directly is to substitute in equation (6) experimental values[9] of $\gamma_{La(NO_3)_3}$ for $\gamma_{Bi(NO_3)_3}$ at the same values of the ionic strength. Not only are these salts of the same charge type but the ionic radii of La^{+++} and Bi^{+++} are not much different, their values[10,11] being 1.15 and 1.0 Å., respectively. The values of K_4 so calculated were extrapolated to $m_{H^+} = 0$ to give $K_4 = 3.2 \times 10^{-3}$. As a final average, $K_4 = 2.8 \times 10^{-3}$ and $\Delta F^0_{298} = 3480$ cal.

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 362, 378.

[10] Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 246.

[11] Aurivillius and Sillén, *Nature*, **155**, 305 (1945).

It is interesting to note that Smith,[4] from his data at higher concentrations and without benefit of activity coefficient corrections, came to the conclusion that the reaction accounting for the solubility of bismuthyl nitrate in nitric acid is one where un-ionized $Bi(OH)(NO_3)_2$ is formed. He discarded this result as "coincidental" in favor of a conclusion from conductivity data that equation (4) represents the true reaction. This agrees with our conclusion.

The $BiO(OH)BiONO_3$–HNO_3 Equilibrium.—No easy explanation appears to exist for the data in Table I which show the solubility of BiO-(OH)-$BiONO_3$ in nitric acid. No single reaction could account for the data.

Acknowledgment.—This research was supported by a fellowship awarded by the E. I. du Pont de Nemours and Company.

EUGENE, OREGON
COLUMBUS, OHIO

RECEIVED FEBRUARY 11, 1950

[CONTRIBUTION FROM THE RADIOCHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Self-Diffusion and Structure of Liquid Water. I. Measurement of Self-Diffusion of Liquid Water with Deuterium as Tracer

BY J. H. WANG[1]

A method for measuring self-diffusion of liquids by means of capillaries is described*; the accuracy of the present method is within about 1%. The self-diffusion coefficients of liquid water in the temperature range 0 to 55° have been determined by both the capillary method and the usual diaphragm cell method with deuterium as tracer. Data of the present work support the quasi-crystalline structure of liquid water and are in contradiction with the assumed existence of definite species of associated water molecules in liquid water. The average apparent activation energy, 4.58 kcal./mole, for self-diffusion of liquid water in the temperature range 10 to 50° indicates that water in this temperature range is only very slightly more than two-coördinated. Below 5°, however, the apparent activation energy of self-diffusion increases appreciably as temperature drops, reaching the approximate value of 6.4 kcal./mole at 0°.

The self-diffusion coefficients of liquid water at various temperatures have been measured independently, by Orr and Butler,[2] Temkin[3] and by Rögener-Leipzig.[4] These measurements are interesting in the light they might throw on the structure of liquid water. However, Orr and Butler's data disagree with the values reported separately by Temkin and by Rögener-Leipzig far beyond the average experimental error reported by either worker. In the present work, the self-diffusion coefficients of liquid water at temperatures in the range 0 to 55° were measured with deuterium as tracer by two different methods. The result shows that Orr and Butler's values are too high.

Principle of Methods

In the first method fine uniform capillaries with lower end sealed were filled with heavy water and held in vertical position in a large circulating bath of pure ordinary water at constant temperature. The deuterium oxide and hydroxide are allowed to diffuse upward, the tracer concentration at the upper end of the capillaries were kept at zero by convection current in the large bath. Under these conditions, the solution of one dimensional linear diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C is concentration of tracer at time t, x the coordinate along which diffusion takes place and D the diffusion coefficient becomes

$$\frac{C}{C_0} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp[-(2n+1)^2\pi^2 Dt/4l^2]\cos\frac{(2n+1)\pi x}{2l} \qquad (2)$$

where C_0 is the initial concentration of tracer, and l is the length of capillary.

The average concentration of solution in the capillary at time t is given by

$$\frac{C_{av}}{C_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2\pi^2 Dt/4l^2] \qquad (3)$$

Values of $C_{av.}/C_0$ are plotted *vs.* Dt/l^2 in Fig. 1.[5]

Thus determination of average tracer concentration in the capillary after diffusion has taken place for a certain time interval t gives the value Dt/l^2, from which D can be readily calculated. The use of fine capillaries to determine self-diffusion coefficient has the special advantage that the measurement is relatively insensitive to slight vibrations or disturbances in the vicinity of the diffusion apparatus as compared to larger capillaries.[6]

In the second method, a slightly modified Northrop[7]–McBain[8] type of diaphragm cell was used. The formula originally developed by Northrop and Anson

$$D = \frac{1}{Kt}\ln\frac{\Delta C_0}{\Delta C} \qquad (4)$$

where K is the cell constant, ΔC_0 and ΔC are the differences in tracer concentrations at time zero and t, respectively, was used in the present calculations.

---

* The measurement of self-diffusion by means of capillaries was first made by J. S. Anderson and K. Saddington (*J. Chem. Soc.*, 5381 (1949)).

(1) Monsanto Post-doctoral fellow, 1949–1950.

(2) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 1273 (1935).

(3) M. Temkin, *Nature*, **136**, 552 (1935).

(4) H. Rögener-Leipzig, *Z. Elektrochem.*, **47**, 164 (1941).

(5) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947.

(6) J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

(7) J. N. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1928).

(8) J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931).