as 1% lower than our values. The authors believe, however, that due to the higher precision attainable today, preparation of the samples by the method of Hudson,[8] and carefully controlled drying conditions, the reported values are worthy of consideration.

Summary

1. A brief description of a precise calorimetric system for measuring heats of combustion and the standardization of the apparatus with a precision of 0.009% have been presented.

2. The heats of combustion, reduced to the standard state $-\Delta U_R$, are reported as: *l*-sorbose, -670.30; β-*d*-levulose, -671.70; α-*d*-galactose, -666.76; β-lactose, -1345.47; β-maltose monohydrate, -1360.50; α-lactose monohydrate, -1354.66 kcal. per mole for the constant pressure process at 25°.

3. A comparison of these results with older values in the literature shows discrepancies of from 0.1-1%.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY]

Equilibria of Mercuric Oxide in Solutions of Dilute Nitric Acid. Evidence for Stepwise Dissociation of Bases

BY A. B. GARRETT AND W. W. HOWELL

Equilibrium data for mercuric oxide in alkali[1] showed no minimum in the mercuric oxide–alkali graph and showed only a very low degree of dissociation for mercuric hydroxide as an acid. This paper presents equilibrium data in *acid* solutions; such data make possible the determination of (1) the position of minimum solubility of mercuric hydroxide, (2) the equilibrium constants of mercuric hydroxide as a base, and (3) the direct evidence for stepwise dissociation of bases. In addition to this, these data, together with the equilibrium data of mercuric oxide in alkali, give the complete record of the behavior of mercuric oxide in dilute solutions of nitric acid and sodium hydroxide.

Procedure.—The general procedure in the determination of the solubility of mercuric oxide in acid was similar to that described by Garrett and Hirschler.[1] The red mercuric oxide used was prepared by the calcination of mercuric nitrate which had been prepared from especially purified mercury and nitric acid. The yellow mercuric oxide was Merck Reagent Quality Mercuric Oxide. The nitric acid was c. p. quality acid. Conductivity water was used for all solutions. All preparations were made in an atmosphere of nitrogen. The temperature was 25.00 ± 0.02°.
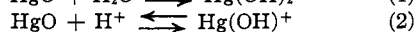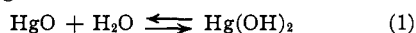
The equilibrium periods, sedimentation periods, method of filtration, and determination of the mercury content of the samples were the same as those described by Garrett and Hirschler.[1]

(1) Garrett and Hirschler, THIS JOURNAL, **60**, 299 (1938).
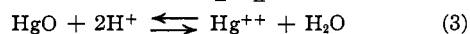
The concentration of acid was determined by preparing the samples with standard solutions of the acid used. The acidity was corrected for the amount of acid used to react with the oxide. The *p*H value of each of the solutions was determined (after equilibrium was established) by means of a glass electrode.

The Data.—The data are given in Tables I and II and in Figs. 1, 2, 3, and 4. All of the data are expressed in moles of mercuric oxide and moles of acid per 1000 g. of water. In most of these data is given the average value of a pair of samples one of which approached equilibrium from undersaturation (u) and the other from supersaturation (s). Several samples, for which the mate was lost, are marked (u) or (s) to indicate the approach to equilibrium.

The data were calculated on the assumption of the following reactions

$$HgO + H_2O \rightleftharpoons Hg(OH)_2 \qquad (1)$$
$$HgO + H^+ \rightleftharpoons Hg(OH)^+ \qquad (2)$$

$$K_2 = \frac{m_{Hg(OH)^+} \gamma_{Hg(OH)^+}}{m_{H^+} \gamma_{H^+}}$$

$$HgO + 2H^+ \rightleftharpoons Hg^{++} + H_2O \qquad (3)$$

$$K_3 = \frac{m_{Hg^{++}} \gamma_{Hg^{++}}}{m_{H^+}^2 \gamma_{H^+}^2} a_{H_2O}$$

The acidity of the standard solutions of which the samples were made was corrected for the acid used in reactions indicated in equations (2) and (3). The curvature of the mercuric oxide–acid graph (Figs. 1, 3, and 4) indicates that reaction (3) is appreciable. While no direct method is

TABLE I

THE SOLUBILITY OF YELLOW MERCURIC OXIDE IN NITRIC ACID

Moles HNO₃/ 1000 g. H₂O as samples were made up	Moles HNO₃/ 1000 g. H₂O corr. for Hg(OH)⁺ and Hg⁺⁺ from values of K_2 = 0.17 and K_3 = 53	Moles HNO₃/ 1000 g. H₂O from glass electrode data (glass electrode value of H⁺ divided by γ_{HNO_3})	Moles HgO/1000 g. H₂O
5.00×10^{-5}	4.0×10^{-5}	3.2×10^{-5}	2.43×10^{-4}
1.00×10^{-4}	1.2×10^{-4}	5.5×10^{-5}	2.57×10^{-4}
2.00×10^{-4}	1.7×10^{-4}	9.5×10^{-5}	2.67×10^{-4}
4.00×10^{-4}	4.0×10^{-4}	2.9×10^{-4}	3.11×10^{-4}
6.00×10^{-4}	5.0×10^{-4}	4.0×10^{-4}	3.35×10^{-4}
8.00×10^{-4}	6.9×10^{-4}	1.5×10^{-3}	3.80×10^{-4}
1.03×10^{-3}	8.2×10^{-4}		4.15×10^{-4}
2.00×10^{-3}	1.5×10^{-3}	1.1×10^{-3}	6.08×10^{-4}
4.00×10^{-3}	2.8×10^{-3}	3.8×10^{-3}	12.1×10^{-4}
6.00×10^{-3}	3.8×10^{-3}		18.3×10^{-4}
8.00×10^{-3}	4.4×10^{-3}		23.2×10^{-4}
1.06×10^{-2}			30.0×10^{-4}
1.56×10^{-2}			50.5×10^{-4}
2.00×10^{-2}	8.4×10^{-3}	8.1×10^{-3}	65.5×10^{-4}
2.00×10^{-2}			68.0×10^{-4}
3.00×10^{-2}			111×10^{-4}
3.00×10^{-2}			108×10^{-4}
4.00×10^{-2}			173×10^{-4}
4.00×10^{-2}			169×10^{-4}
5.00×10^{-2}	1.0×10^{-2}		217×10^{-4}
5.85×10^{-2}	1.0×10^{-2}		236×10^{-4}
6.00×10^{-2}			253×10^{-4}
6.34×10^{-2}	1.4×10^{-2}		262×10^{-4}
6.83×10^{-2}	1.3×10^{-2}		299×10^{-4}
7.00×10^{-2}			312×10^{-4}
7.03×10^{-2}	1.3×10^{-2}		312×10^{-4}
7.22×10^{-2}	1.3×10^{-2}		329×10^{-4}
7.43×10^{-2}	1.3×10^{-2}		333×10^{-4}
7.61×10^{-2}	1.3×10^{-2}		349×10^{-4}
7.80×10^{-2}	1.2×10^{-2}		362×10^{-4}
9.76×10^{-2}	1.6×10^{-2}		449×10^{-4}
1.17×10^{-1}	1.4×10^{-2}		536×10^{-4}
1.37×10^{-1}			638×10^{-4}
1.40×10^{-1}	1.8×10^{-2}		596×10^{-4}
1.56×10^{-1}	2.3×10^{-2}		718×10^{-4}
1.60×10^{-1}	1.9×10^{-2}		662×10^{-4}

TABLE II

THE SOLUBILITY OF RED MERCURIC OXIDE IN NITRIC ACID

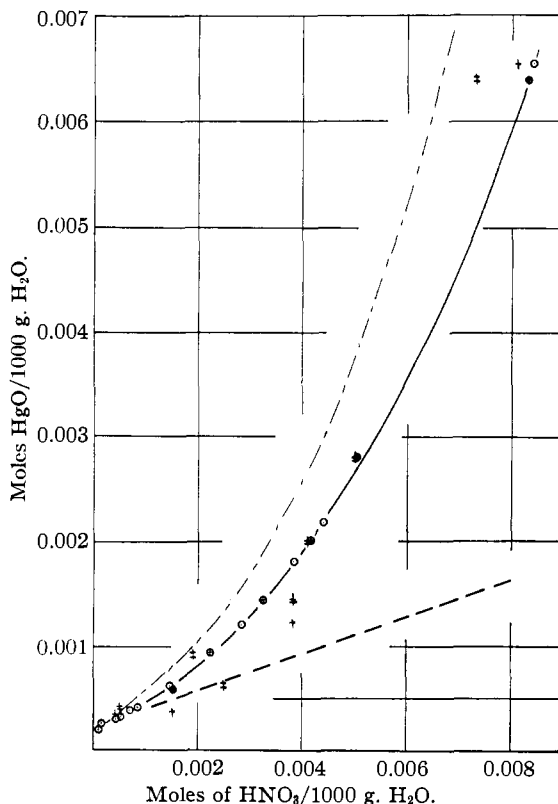| Moles HNO₃/ 1000 g. H₂O as samples were made up	Moles HNO₃/ 1000 g. H₂O corr. for Hg(OH)⁺ and Hg⁺⁺ from values of K_2 and K_3	Moles HNO₃/ 1000 g. H₂O from glass electrode data (glass electrode value of H⁺ divided by γ_{HNO_3})	Moles HgO/1000 g. H₂O
1.00×10^{-4}	3.8×10^{-4}	1.4×10^{-4}	2.98×10^{-4}
2.00×10^{-4}	4.6×10^{-4}	0.7×10^{-4}	3.14×10^{-4}
3.00×10^{-4}	2.8×10^{-4}	1.4×10^{-4}	2.77×10^{-4} (u)
5.00×10^{-4}	6.1×10^{-4}	3.0×10^{-4}	3.48×10^{-4} (s)
7.00×10^{-4}	6.6×10^{-4}	3.8×10^{-4}	3.56×10^{-4}
9.00×10^{-4}	8.1×10^{-4}	4.8×10^{-4}	4.02×10^{-4} (u)
2.00×10^{-3}	1.5×10^{-3}	2.5×10^{-3}	6.32×10^{-4}
3.00×10^{-3}	2.2×10^{-3}	1.9×10^{-3}	9.17×10^{-4}
5.00×10^{-3}	3.2×10^{-3}	3.8×10^{-3}	14.2×10^{-4}
7.00×10^{-3}	4.0×10^{-3}	4.1×10^{-3}	20.2×10^{-4}
9.00×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	27.9×10^{-4}
2.00×10^{-2}	8.3×10^{-3}	7.3×10^{-3}	64.2×10^{-4} (s)

Fig. 1.— — – —, limiting value if all mercury were in the form Hg⁺⁺ as indicated by equation (3); — — —, amount of Hg(OH)⁺ present; ‡†, glass electrode values; ⊙, calculated values from K_2 and K_3.

readily available to determine $m_{Hg^{++}}$ it can be determined together with the $m_{Hg(OH)^+}$ by a method of approximation with the aid of a relationship of activity coefficients similar to that derived for the dissociation of copper hydroxide.[2] Assuming that the total solubility of the mercuric oxide (S_{HgO}) is expressed by the equation

$$S_{HgO} = m_{Hg(OH)_2} + m_{Hg(OH)^+} + m_{Hg^{++}} \qquad (4)$$

where $m_{Hg(OH)_2}$ is the undissociated mercuric hydroxide (essentially water solubility since Hg(OH)₂ is only slightly dissociated[1])

$$m_{Hg(OH)^+} = K_2 \frac{m_{H^+} \gamma_{H^+}}{\gamma_{Hg(OH)^+}}$$

(2) Johnston and McDowell, THIS JOURNAL, **58**, 2009 (1936). The use of this relationship is necessary here since $\gamma_{Hg^{++}}$ has not been determined. An alternative procedure at this point would be to use the value of the activity coefficient for an ion similar to Hg⁺⁺. A probable choice would be $\gamma_{Pb^{++}}$ from the data of $\gamma_{Pb(NO_3)_2}$ given by Randall and Vanselow, *ibid.*, **46**, 2448 (1924).

and

$$m_{Hg^{++}} = K_3 \frac{m_H^2 {}_{+} \gamma_H^2 {}_{+}}{\gamma_{Hg^{++}}} \times \frac{1}{a_{H_2O}}$$

Then

$$S_{HgO} = m_{Hg(OH)_2} + K_2 \frac{m_{H^+} \gamma_{H^+}}{\gamma_{Hg(OH)^+}} +$$
$$K_3 \frac{m_{H^+}^2 \gamma_{H^+}^2}{\gamma_{Hg^{++}}} \times \frac{1}{a_{H_2O}} \quad (5)$$

which can be simplified to the following equation with the aid of the relationship of activity coefficients referred to above and also assuming $\gamma_{H^+}/\gamma_{Hg(OH)^+} = 1$ at low and moderate values of the ionic strength.

$$S_{HgO} = m_{Hg(OH)_2} + K_2 m_{H^+} +$$
$$K_3 m_{H^+}^2 \left(\frac{1}{\gamma_{HNO_3}^2}\right) \left(\frac{1}{a_{H_2O}}\right) \quad (6)$$

The terms in parentheses (equation 6) can be evaluated from reliable data[3] and from Raoult's law, respectively.
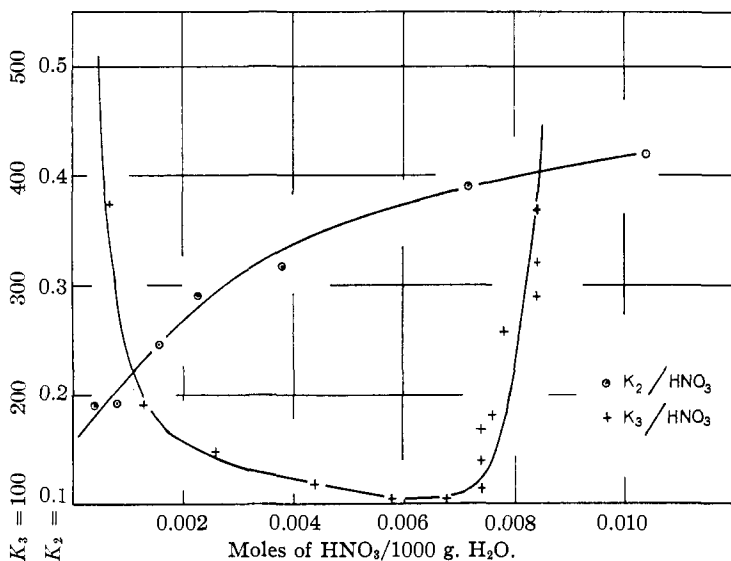

Fig. 2.

The values of K_2 and K_3 were first determined by assuming as first approximation that reactions (2) and (3) proceed to the same extent; the acid concentrations were corrected for the amount used in the reactions with HgO; K_2 and K_3 were then evaluated by solution of simultaneous equations (using equation 6). This procedure was repeated until constant values of K_2 and K_3 were obtained. As a critical test of this method, this whole procedure was again repeated on the assumption that reaction (2) was the only effective reaction and the value of the acidity was corrected

accordingly. This method gave approximately the same values of K_2 and K_3 as the first procedure.

An indication of the limiting value of K_2 and K_3 was obtained by the independent calculation of K_2 and K_3 assuming, in the calculation of K_2, that reaction (3) did not take place, and, in the calculation of K_3, that reaction (2) did not take place. These values of K_2 and K_3 were then plotted against the concentration of acid (see Fig. 2). It is obvious that at low concentrations the ratio of K_2/m_{HNO_3} should be constant. Extrapolation of the K_2/m_{HNO_3} graph indicates a value of $K_2 > 0.1$ and < 0.2 at $m_{HNO_3} = 0$. This justifies the magnitude of the value of $K_2 = 0.17$ determined by the method of approximations described above. The value of K_3 could not be determined graphically as readily as that of K_2 due to an apparent theoretical buffering action occurring at approximately $m_{HNO_3} = 0.008$ (see Fig. 2). This graph does indicate the limits of acid concentration through which the value of K_2 and K_3 can be calculated reliably; furthermore, it suggests a limiting value in the magnitude of 100 for K_3 which is in agreement with the value of $K_3 = 53$ from the method of approximations. Additional information given by Fig. 2 is the fact that the drift in the values of K_2 and K_3 indicates clearly that neither reaction (2) alone nor reaction (3) alone is sufficient to account for the solubility of mercuric oxide in nitric acid. The alternative is that the dissociation of mercuric hydroxide must be a stepwise dissociation process; such a process was suggested by Kolthoff,[4] who observed from data in cell reactions that "Wanneer nu de dissociatie van het kwikhydroxyde totaal volgens folgende vergelijking plaats had: $Hg(OH)_2 = Hg^{++} + 2OH^-$, zou $[Hg^{++}] = \frac{1}{2}[OH^-]$ zijn.

"Uit de genoemde waarden blijkt daarentegen, dat $[Hg^{++}]$ veel kleiner is, en dat de dissociatie, die wel is waar zeer gering is, hoofdzakelijk a.v. plaats heeft: $Hg(OH)_2 = Hg(OH)^+ + OH^-$."

"If now the total dissociation of $Hg(OH)_2$ took place according to the following equation $Hg(OH)_2 \rightleftarrows Hg^{++} + 2OH^-$ then $[Hg^{++}]$ should be equal to $\frac{1}{2}(OH)^-$ but from the values given it is evident on the other hand that the Hg^{++} is much

(3) Abel, Redlich and Lengyel, Z. physik. Chem., **132**, 189 (1928).

(4) Kolthoff, Chem. Weekblad, **14**, 1016 (1917).

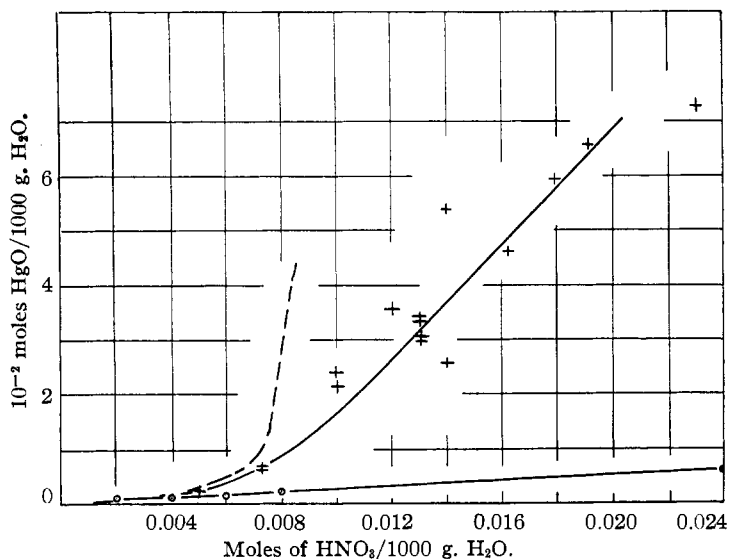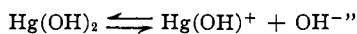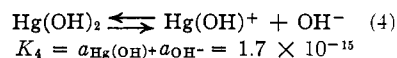smaller and that the dissociation, which is probably very small, takes place chiefly as follows

$$Hg(OH)_2 \rightleftharpoons Hg(OH)^+ + OH^-"$$

Fig. 3.— — — — — , limiting value assuming all the mercury is in the form of Hg^{++} [see equation (3)]; +, glass electrode values; ⊙, values from concentration of standard acid with which the samples were made up.

Our method of treatment of the data, however, gives *direct* evidence of a stepwise dissociation process for bases. Figure 1 shows the agreement between the calculated values of nitric acid and those measured by means of the glass electrode. This graph also shows the limiting value of m_{HgO}/m_{HNO_3} assuming that all of the mercuric oxide may be in the form Hg^{++}. Figure 3 gives a similar comparison of this limiting value with that obtained by glass electrode measurements at higher concentrations. These graphs (Figs. 1 and 3) are direct evidence of the fact that mercuric hydroxide dissociates in a stepwise manner.

The calculated values of nitric acid (calculated from K_2 and K_3) show excellent agreement with the glass electrode values to $m_{HNO_3} = 0.008$ (see Fig. 1). Efforts to obtain values of K_2 and K_3 to fit the curve above this value were fruitless. This may be due to too small a value of K_3—however, a larger value of K_3 disturbed the agreement of the data at the low concentration where the limiting law would be most applicable. It

may well be assumed that above $m_{HNO_3} = 0.008$ the solubility of the mercuric oxide becomes so high that the activity coefficient relationship[2] used to simplify the expression for K_3 is no longer valid; also the assumption that the ratio $\gamma_{H^+}/\gamma_{Hg(OH)^+} = 1$ may not be valid in this high solubility range. If, however, the lack of fit is due to an incorrect value of K_3, it can be observed here that the value of K_3 *could not* be greater than 100 nor less than 53. We believe the former reason is the more probable explanation.[5]

The values of K_2 and K_3 can be converted to the respective ion products and ionization constants by the use of the ion product of water and the value of $a_{Hg(OH)_2} = 2.4 \times 10^{-4}$ (see Ref. 1), and will give the following values for the reactions

$$Hg(OH)_2 \rightleftharpoons Hg(OH)^+ + OH^- \quad (4)$$
$$K_4 = a_{Hg(OH)^+}a_{OH^-} = 1.7 \times 10^{-15}$$

and

$$K_4' = \frac{a_{Hg(OH)^+}a_{OH^-}}{a_{Hg(OH)_2}} = 7.1 \times 10^{-12}$$

and

$$Hg(OH)_2 \rightleftharpoons Hg^{++} + 2OH^- \quad (5)$$
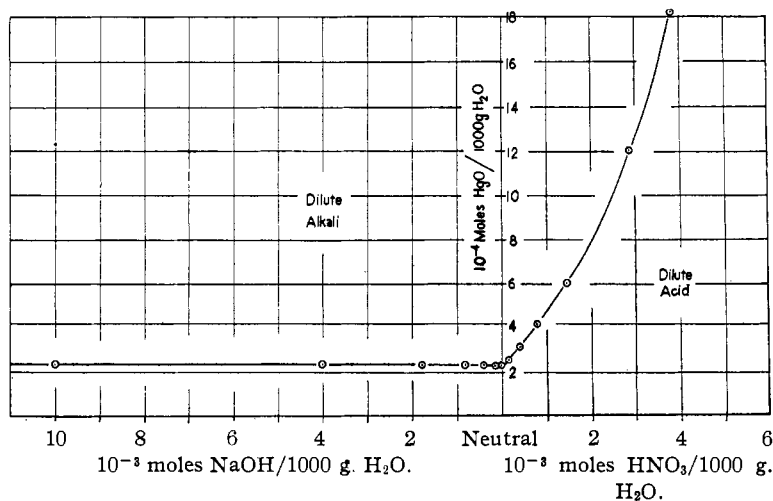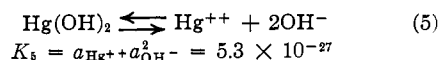$$K_5 = a_{Hg^+}a_{OH^-}^2 = 5.3 \times 10^{-27}$$

Fig. 4.

and

$$K_5' = \frac{a_{Hg^+}a_{OH^-}^2}{a_{Hg(OH)_2}} = 2.2 \times 10^{-23}$$

(5) Another possible explanation is that another equilibrium may be involved in addition to those considered here. This is possible due to the notoriously unpredictable characteristics of mercury compounds. The more probable explanation, however, lies in the uncertainty of the value of the activity coefficients.

The corresponding values calculated by Kolthoff at 18° are

$$K_4' = 5.35 \times 10^{-11}$$
$$K_5' = 7.38 \times 10^{-23}$$

An interesting fact with respect to mercuric oxide is that the position of minimum solubility appears to be that in water solution (see Fig. 4 which includes data given by Garrett and Hirschler[1]). This is to be expected since Kolthoff has indicated that the pH of water solutions of mercuric oxide at 18° is approximately 7.2. It is also to be observed that the value[1] of K_6 for the reaction

$$H_2HgO_2 \rightleftharpoons H^+ + HHgO_2^- \qquad (6)$$
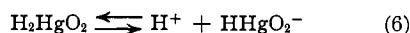
is

$$K_6 = 1.4 \times 10^{-15}$$

and the ion product is 3.4×10^{-19}; while the value of K_4' for the reaction

$$Hg(OH)_2 = Hg(OH)^+ + OH^- \qquad (4)$$
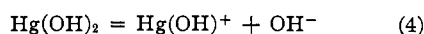
is

$$K' = 7.1 \times 10^{-12}$$

and the ion product is 1.7×10^{-15}. The similar magnitude of K_4' and K_6 and of the ion products of these two reactions is further evidence of a nearly neutral hydroxide and therefore one which would be expected to give its minimum solubility at approximately pH = 7. In fact both the m_{H^+} and the m_{OH^-} contributed by the mercuric hydroxide are less than the concentration of these ions produced by water; however, the $m_{OH^-} > m_{H^+}$. This indicates the minimum solubility might be expected to be slightly on the basic side. These very low values of m_{H^+} and m_{OH^-} contributed by the dissociation of mercuric hydroxide serve to explain the fact that the conductivity of aqueous solutions of mercuric oxide is about that of the solvent itself.

The character of the solid phase was established by analysis for the nitrate ion and for the mercury content, respectively. This was particularly necessary at the high acid concentration where one might expect basic salt formation. The solid phase was separated from the mother liquor by filtration; it was washed quickly in the filter crucible with two small portions of water to remove adsorbed nitric acid and analyzed with standard potassium iodide solution. All samples except one analyzed to mercuric oxide and gave negative nitrate tests.

Summary

The solubility of mercuric oxide has been determined in nitric acid solutions ranging from 0.00005 to 0.16 molal. The constants for the dissociation of mercuric hydroxide have been evaluated from these data. The values of these constants are in good agreement with the fact that mercuric hydroxide solutions have a very low conductivity and give a pH value of approximately 7. They are also in agreement with similar constants obtained from e. m. f. measurements (Kolthoff). The data indicate that the minimum solubility is in water solutions, that mercuric hydroxide dissociates in a stepwise manner, and that the H$^+$ and OH$^-$ contributed by mercuric hydroxide in water solution are less than those contributed by the solvent.

The Viscosity Function. II.[1] Viscosity and Constitution

BY ERNEST P. IRANY

The graphical method of analyzing viscosity data by means of functional viscosity scales has revealed a great number of general regularities in the dependency of viscosity on temperature, volume (ideal dilution) and pressure. One may reasonably expect some relation between viscosity and chemical constitution to be derivable by the same or analogous means.

However, before this can be attempted it is

(1) The first paper on the subject appeared in THIS JOURNAL, **60**, 2106 (1938).

important to realize the difficulties arising from the uncertainty which still surrounds the concepts to be dealt with. We are not yet able to define the liquid state or to recognize the real meaning of constitution within it. Molecules, as described by their chemical formula, exist in gases but not in the crystal lattices of solid bodies; all that can be said about liquids is that their molecules must be in some intermediate condition: neither as mobile and independent as in gases nor as fixed and diffused as in solids. Precisely what