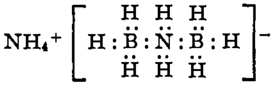
ment was completed in forty hours at −80°. The entire original sample of methyl ether was then regained in pure condition, leaving a solid having the same composition as the diammoniate of diborane. Its identity with that substance was now clearly recognized by its stability at room temperature, its reaction with sodium in liquid ammonia at −75° to produce 3.97 cc. (1.02 equivalents per mole of diborane) of hydrogen during thirty minutes, and even by the characteristic formation of an exceedingly light and porous solid web when the ammonia was sublimed away after the completion of the reaction with sodium.

Acknowledgment.—We wish to express our thanks to the National Research Council and to the Research Corporation, for providing the liquid nitrogen used in this work.

Summary

The reaction of diborane with ammonia at low temperatures is interpreted as an addition of borine (BH_3) to ammonia, followed by other reactions leading to a final product having the structure  $\mathrm{NH_4^+}\left[\begin{array}{c}\mathrm{H\ \ H\ \ H}\\ \mathrm{H:\overset{..}{\underset{..}{B}}:\overset{..}{\underset{..}{N}}:\overset{..}{\underset{..}{B}}:H}\\ \mathrm{H\ \ H\ \ H}\end{array}\right]^-$. These ideas are supported by the following new experimental facts.

1. The product reacts with sodium in liquid ammonia (at −77°) to produce one equivalent of hydrogen per mole of diborane involved; it thus seems to contain one ammonium ion per pair of boron atoms.

2. A slow secondary reaction of the product with ammonia and sodium, yielding barely 40% more hydrogen, is easily explained by assuming that ammonia removes a BH_3 group from the above structure, by a reversible reaction producing $NH_4BH_3NH_2$. This explanation is supported by the fact that trimethylamine reacts with the "diammoniate of diborane" to give borine trimethylammine. Neither reaction is easily explained by other structures.

3. The reaction of the new compound $(CH_3)_2OBH_3$ with ammonia and sodium produces the salt $NaBH_3NH_2$. The negative ion of this salt is considered to be an intermediate step in the formation of the above structure.

4. The salt $NaBH_3NH_2$ strongly absorbs diborane. This fact justifies the assumption that the negative ion of the above structure is easily formed by addition of BH_3 to the $BH_3NH_2^-$ ion, and is capable of stable existence.

5. The new compound B_2H_7N, having the structural skeleton B–N–B, is easily prepared from the "diammoniate of diborane."

CHICAGO, ILL. RECEIVED NOVEMBER 29, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Solubilities of Red and Yellow Mercuric Oxides in Water, in Alkali, and in Alkaline Salt Solutions. The Acid and Basic Dissociation Constants of Mercuric Hydroxide

BY A. B. GARRETT AND ALFRED E. HIRSCHLER[1]

This investigation had its inception in an effort to obtain data for mercuric oxide similar to those obtained in this Laboratory for silver oxide[2] and for cupric oxide,[3] to establish the amphoteric character of mercuric oxide, to obtain information concerning the nature of the mercury-bearing ions in solution, to determine the dissociation constants of mercuric hydroxide, and to calculate therefrom the free energy changes in a number of reactions involving mercuric oxide.

Solutions of mercuric oxide in alkali were thought to be colloidal by Chatterji and Dhar.[4] Fuseya,[5] however, measured the solubility of red mercuric oxide in several concentrations of sodium hydroxide ranging from 0.01 to 2 *M;* the results indicated that a true chemical reaction was responsible for the solubility. Due to an obvious error, the solubilities listed by Fuseya are 100 times too great.

There is a rather serious discrepancy in the work of Fuseya, for the extrapolation of the alkali solubility to zero alkali concentration leads to a solubility value larger than the solubility of the oxide in pure water. Fuseya explains this discrepancy by supposing that the oxide is peptized by dilute alkali to finer particles, which might be

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[1] Present address: The Sun Oil Laboratories, Norwood, N. J.

[2] Johnston, Cuta and Garrett, THIS JOURNAL, **55**, 2311 (1933).

[3] McDowell and Johnston, *ibid.*, **58**, 2009 (1936).

[4] Chatterji and Dhar, *Chem. News*, **121**, 253 (1920).

[5] Fuseya, THIS JOURNAL, **42**, 368 (1920).

expected to show a greater solubility, since he observed that after a few hours of shaking in alkali, the oxide became yellow in color. Repetition of this work is therefore desirable, employing a more accurate analytical method for mercury as well as extending the solubility determinations into more dilute alkali, in order to investigate the possible existence of a minimum in the solubility curve. It appeared interesting, in the light of Fuseya's observations, to determine the solubility of yellow mercuric oxide as well. It was hoped that these results would throw some light on the much debated question of the allotropy of the red and yellow forms of mercuric oxide.

Experimental

The general manipulations and solubility apparatus were the same as employed by Johnston, Cuta and Garrett[2] in a similar study of silver oxide. The work was carried out in an atmosphere of purified nitrogen.

Mercuric nitrate, for the preparation of oxides, was prepared by dissolving redistilled reagent quality mercury in nitric acid and partially crystallizing the resulting solution.

Barium hydroxide used in precipitation of the oxides, was recrystallized five times from conductivity water.

Red mercuric oxide was prepared by (1) thoroughly washing Baker and Adamson reagent quality red mercuric oxide in hot and cold conductivity water for periods of at least four weeks; (2) by ignition of the pure nitrate, prepared as described above, on a sand-bath until completely decomposed, and the resulting product washed (preparation R-3, R-5); and (3) by dropping 0.05 *M* solutions of pure mercuric nitrate and barium hydroxide, simultaneously, into 500 cc. of boiling water or dilute alkali solution, in an apparatus similar to that described by Johnston, Cuta and Garrett. The entire process, including subsequent washings (30–40 in number), was carried out in an atmosphere of nitrogen. Oxide (2) gave reproducible solubilities; oxide (1) very erratic values, 50–100% high; and oxide (3) erratic values ranging 5–10% higher than the yellow oxide.

Yellow mercuric oxide was prepared by (1) thoroughly washing Baker and Adamson reagent quality yellow oxide in conductivity water (preparations Y-1, Y-4, Y-5); and (2) by precipitation under various conditions in the cold in the apparatus used for preparation of the red oxide (preparations Y-9, Y-10).

It was found necessary to maintain a slight excess of alkali at all times, and to employ a fairly rapid rate of precipitation in order to obtain a satisfactory product. The various preparations differed considerably in color and particle size (as determined by microscopic examination) but were found to have solubilities identical with the Baker and Adamson product. For this reason, the latter was used for the greater part of this work.

Great care was exercised throughout to eliminate, so far as possible, an abnormal solubility due to very fine particles. This was accomplished by storing the oxides under conductivity water, allowing the oxides to stand at least several weeks before using; by numerous washings, using both hot and cold conductivity water, decanting quickly each time in order to get rid of the finer particles, and by shaking the samples from three to six weeks in alkali to approach equilibrium.

Potassium and sodium hydroxides at concentrations below 1 *N* were prepared from pure amalgams in the manner described by Johnston, Cuta and Garrett. At concentrations greater than 1 *N*, the alkalies were prepared by precipitation of the carbonate from solutions of the reagent quality materials by the addition of barium hydroxide. Lithium hydroxide was prepared by dissolving Merck reagent in conductivity water and allowing the slight precipitate to settle.

The salts used were recrystallized two to four times from conductivity water from reagent quality materials.

Conductivity water was used in the preparation of all solutions, and in the washing and purification of all materials. The conductivity of this water varied between 1–1.4 × 10^{-6} mho.

Equilibrium was approached both from undersaturation (u) and from supersaturation (s). Samples of mercuric oxide and alkali of a known concentration were made up in pairs and sealed in 200-cc. nitrogen filled flasks by means of an oxyhydrogen torch. One sample of each pair was shaken in a thermostat at 25 ± 0.01° for approximately three weeks; the other sample was agitated at 42° for two to four days, then transferred to the 25° thermostat for an additional three week period. Following the shaking period, the samples were allowed to sediment for three to five days before analysis, in order to allow ample time for all suspended material to settle.

Analytical Procedure

The clear solutions were decanted by nitrogen pressure through a G3 Jena sintered glass filter, in such a way that contact with the air was avoided, and analyzed for alkali and mercury content. The first 30 cc. to pass through the filter was discarded. The alkali concentration was determined by weight titration to the first color change of methyl orange. The end-point error was corrected. All weighings were reduced to vacuum. Corrections for the neutralizing value of the bi-mercurate ion are not significant at any concentration studied.

For the analysis of mercury, a refinement of the potentiometric method suggested by Maricq[6] was employed in which the mercury is titrated with potassium iodide, the potential variations being followed by means of an amalgamated platinum electrode and a calomel reference cell. Titrations were carried out in a 250-cc. beaker, connected to the reference cell by a bridge of potassium nitrate set in agar agar. Instead of using a potentiometer, a Leeds and Northrup galvanometer of sensitivity 3 × 10^{-9} amp./cm. was connected directly through a resistance of 10^6 ohms to the titration cell. The scale was placed 4.5 meters from the galvanometer for greater sensitivity. Efficient mechanical stirring was provided.

After a preliminary study of the effect of acid or salt concentration, rate of addition of reagents, treatment of electrode, etc., it was found that 1 mg. of mercury in 100 cc. of solution could be analyzed with a reproducibility of

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[6] Maricq, *Bull. soc. chim. belg.*, **37**, 241 (1928).

0.1 to 0.2% in solutions of low or moderate salt concentration, and that in concentrated solutions of sodium nitrate, potassium nitrate, sodium sulfate or barium nitrate, the analysis differed from that in dilute solution by less than 0.5%. The following procedure was adopted.

Five drops of 0.1 *N* sulfuric acid were added to the sample after titration to the first color change of methyl orange, and the solution diluted to 100 cc. with conductivity water. The electrode, a 1 in. (2.5 cm.) square of platinum foil, was scrubbed with pumice, dipped into cleaning solution, washed, and amalgamated by electrolysis. After starting the stirring motor, 10 cc. of 0.001 *N* potassium iodide was added by a calibrated pipet, at a rate of 4–5 drops/sec. Titration was completed with the same reagent from a microburet. Two minutes were allowed for the attainment of equilibrium. Near the end-point, the potassium iodide was added in drops of 0.02 cc. Except in solutions of high salt content, the end-point could be located easily by inspection to 0.01 cc.

The ultimate standards for the determination of mercury were solutions of mercuric nitrate about 0.0014 *N*, prepared by dissolving a weighed amount of pure mercury in redistilled nitric acid and diluting to one liter in a volumetric flask. The 0.001 *N* potassium iodide solutions prepared from twice recrystallized reagent quality potassium iodide and conductivity water, were standardized against the mercury solutions under conditions closely identical with those employed in the analysis of samples. The end-point was found to vary not more than 0.2% from the stoichiometric point for the formation of mercuric iodide.

Salt concentrations were not determined by analysis. Alkaline salt solutions were made up by weight from standard solutions of the salts and of the alkali, and the oxide washed four times with this solution before sealing up.

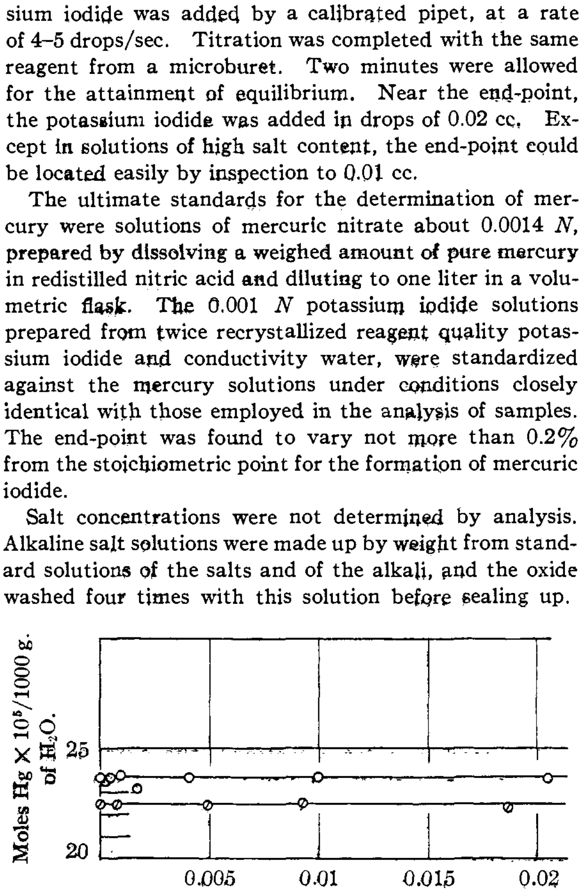

Fig. 1.—Solubility of red and yellow mercuric oxide in very dilute alkali: O, yellow oxide, ⊘, red oxide.

Solutions more dilute than 0.02 *N* alkali were analyzed in the following manner: a 0.005 *N* standard solution of carbonate-free sodium hydroxide was prepared, and an approximately 0.013 *N* solution of sulfuric acid was empirically standardized against this alkali for amounts of alkali ranging from 2–50 cc. Two drops of phenolphthalein indicator were added in each case. The apparent strength of the acid used was plotted against the number of cc. of acid used in the titration, and a smooth curve drawn through the points. A microburet was employed. After analyzing a sample, the proper value to employ for the acid strength was read from the curve. The total volume of solution was kept at about 100 cc. in each case. This procedure obviated the necessity of a rather uncertain calculation of end-point error.

These empirical standardizations were made, and the analyses carried out, in a 250-cc. beaker tightly covered with a section cut from a No. 13 rubber stopper, provided with holes for the microburet, a mechanical stirrer, and for a tube through which a stream of carbon dioxide-free nitrogen was passed during the analysis. The beaker was filled with nitrogen before adding the sample, and immediately replaced under the cover. By this means it was found possible to analyse 0.0005 *N* alkali solutions with an error of less than 5%.

The Solubility Data

The results obtained are given in the following tables in which all concentrations are expressed in moles per 1000 g. of water. The data also are illustrated in the accompanying figures. Each solubility value in the tables and on the graphs is the average of the values of a pair of samples, prepared as described above, one of which was allowed to approach equilibrium from undersaturation (u) and the other from supersaturation (s). In a few cases the mate to a pair was lost and a single value of the solubility is listed with the symbol (s) or (u) to indicate the previous history of that sample. The separate solubility values were within ±2% of the pair average with but one exception; and 75% of the data were within ±1% deviation from the pair average.

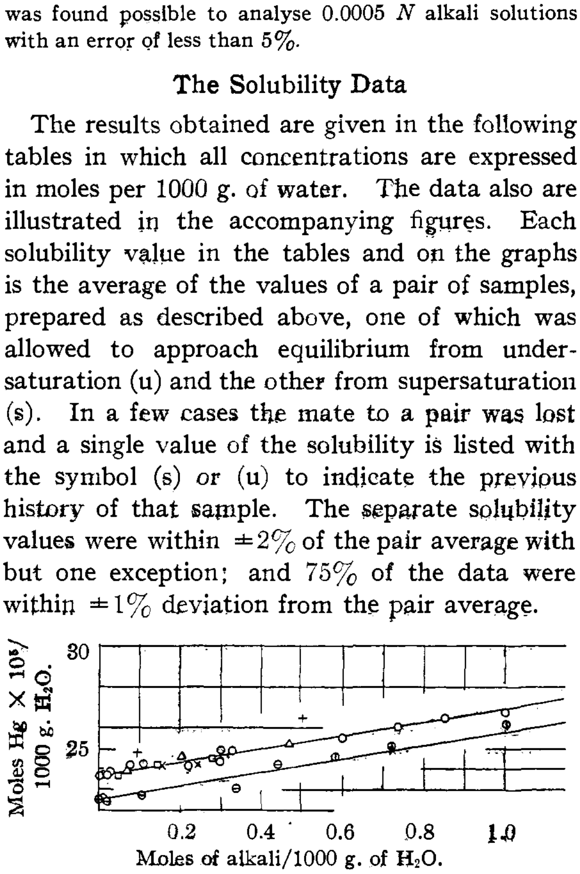

Fig. 2.—Solubility of red and yellow mercuric oxide in alkali from 0–1.0 *N*. Yellow oxide: O, Prepns. Y-1, Y-4, Y-5, NaOH; ×, Prepns. Y-9, NaOH; □, Prepns. Y-10, NaOH; △, Prepns. Y-1, LiOH; +, Fuseya. Red oxide: ◑, Prepns. R-3, NaOH; ⊖, Prepns. R-5, NaOH.

The Solubility of Mercuric Oxide in Conductivity Water

The solubility values in the literature for the red oxide are 23.7,[7] 23.0,[8] and 23.4[5] × 10^{-5} mole Hg/1000 g. H_2O, and for the yellow oxide there is only the value 23.9 × 10^{-5} mole Hg/1000 g. H_2O.[7] Because of the more accurate analytical method used in the present investigation, we believe the values 22.5 × 10^{-5} and 23.7 × 10^{-5} mole Hg/1000 g. H_2O are more reliable for the

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[7] Schick, *Z. physik. Chem.*, **42**, 155 (1903).

[8] Hulett, *ibid.*, **37**, 385 (1901).

water solubilities of the red and yellow oxides, respectively. Additional support is given these values by the consideration that since the basic ionization of mercuric hydroxide is so small (this is discussed in a later section), the extrapolated value for the alkali solubilities is probably more reliable for the water solubility than that directly measured. In this case the measured solubilities and the extrapolated values are identical for both red and yellow oxides.

TABLE I

YELLOW MERCURIC OXIDE

Oxide prepn.	Hg/1000 g. $H_2O \times 10^5$ pair average
Y 1	23.5
Y 4	23.9
Y 5	23.8
Y 9	23.6

Average 23.7 × 10^{-5} mole Hg/1000 g. H_2O

TABLE II

RED MERCURIC OXIDE

Oxide prepn.	Hg/1000 g. $H_2O \times 10^5$ pair average
R 3	23.1
R 5	22.5
R 5	22.5^u
R 5	22.5

TABLE III

THE SOLUBILITY OF REAGENT QUALITY YELLOW OXIDE IN SODIUM HYDROXIDE

Moles of alkali/ kg. H_2O	Hg/kg. $H_2O \times 10^5$ pair average	Moles of alkali/ kg. H_2O	Hg/kg. $H_2O \times 10^5$ pair average
0.00010	23.4	.8515	26.5
.00042	23.7	1.006	26.8
.00082	23.8	1.512	28.2
.0018	23.2	1.776	28.4
.0040	23.7	2.057	28.7s
.0100	23.7u	2.562	29.6
.0207	23.7	3.263	31.8u
.0290	23.9u	3.405	30.6u
.0770	24.2u	3.940	31.6
.0944	24.3	4.460	31.2
.1015	24.4	5.046	32.2
.1074	24.3	5.952	31.1
.1506	24.3u	Sample Y-10 in NaOH	
.2230	24.1	0.0477	23.7
.3022	24.9	.1448	24.2
.3467	24.9	.2776	24.5
.5169	24.8u	Sample Y-9 in NaOH	
.5995	25.5	0.1513	24.2
.7372	26.1	.2438	24.2

TABLE IV

THE SOLUBILITY OF REAGENT QUALITY YELLOW OXIDE IN POTASSIUM HYDROXIDE AND LITHIUM HYDROXIDE

Moles of alkali /kg. H_2O	Hg/kg. $H_2O \times 10^5$ pair average
KOH	
0.1082	24.0
.3038	24.3
.8175	25.3
LiOH	
0.0689	23.9
.2019	24.6
.4667	25.2

TABLE V

THE SOLUBILITY OF REAGENT QUALITY YELLOW OXIDE IN ALKALINE SALT SOLUTIONS

Moles of alkali /kg. H_2O	Hg/kg. $H_2O \times 10^5$ pair average	Salt molality	Total ionic strength
KNO_3–NaOH			
0.1361	29.1	0.8143	0.950
.1789	33.7	1.725	1.906
.1328	38.4	2.400	2.533
$NaNO_3$–NaOH			
0.1462	32.6	1.072	1.218
.1738	49.6s	2.637	2.811
.1682	75.3	6.397	6.565
Na_2SO_4–NaOH			
0.1433	30.1	0.5863	1.901
.1380	34.7	1.145	3.573
.1649	37.0	1.668	5.162
.1454	39.0	2.137	6.556

TABLE VI

THE SOLUBILITY OF RED MERCURIC OXIDE IN SODIUM HYDROXIDE

Moles of alkali /kg. water	Hg/kg. $H_2O \times 10^4$ pair average
0.00088	22.5
.0050	22.5
.0093	22.6
.0187	22.4
.1064	22.7s
.3398	23.1
.4406	24.2s
.5818	24.6
.7223	25.1u
1.001	26.2
1.638	27.2
1.987	27.6u
2.940	29.4
3.956	29.7
4.936	29.8

Discussion and Interpretation of Results

If we can correctly regard mercuric hydroxide as amphoteric, its aqueous solubility may be interpreted in terms of the following equilibria, whose relative importance in determining the solubility will depend on the *p*H of the solution. In acid or neutral solution the reaction

$$HgO + H_2O = Hg(OH)_2 = Hg^{++} + 2OH^- \quad (1)$$

will predominate, while the reactions (expressed in terms of the classical acid–base theory)

$$HgO + OH^- = HHgO_2^- \quad (2)$$
$$HgO + 2OH^- = HgO_2^= + H_2O \quad (3)$$

will become increasingly more important as the alkali concentration increases.

We may arbitrarily select the red form of the oxide as representing the standard state at atmospheric pressure. For the red oxide, then, the equilibrium constants corresponding to equations (2) and (3) become

$$K_2 = (m_{\mathrm{HHgO_2^-}}/m_{\mathrm{OH^-}})(\gamma_{\mathrm{HHgO_2^-}}/\gamma_{\mathrm{OH^-}})$$
$$K_3 = (m_{\mathrm{HgO_2^-}}/m^2_{\mathrm{OH^-}})(\gamma_{\mathrm{HgO_2^-}}/\gamma^2_{\mathrm{OH^-}})a_{\mathrm{H_2O}}$$

where the *m*'s represent stoichiometric molalities of the ions; the γ's their corresponding activity coefficients, and $a_{\mathrm{H_2O}}$ represents the activity of water from the solutions. The total solubility of mercury at concentrations of alkali too great to permit the existence of $\mathrm{Hg^{++}}$ ions is given by the relationship

$$S_{\mathrm{Hg}} = m_{\mathrm{Hg(OH)_2}} + K_2m_{\mathrm{OH^-}}\ (\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{HHgO_2^-}}) \\ + K_3m^2_{\mathrm{OH^-}}\ (\gamma^2_{\mathrm{OH^-}}/\gamma_{\mathrm{HgO_2^-}})\ 1/a_{\mathrm{H_2O}} \quad (4)$$

where $m_{\mathrm{Hg(OH)_2}}$ represents an assumed constant concentration of non-dissociated mercuric hydroxide in equilibrium with the solid phase.

This equation may be considerably simplified. Following the treatment suggested by McDowell and Johnston,[3] equation (4) becomes

$$S_{\mathrm{Hg}} = m_{\mathrm{Hg(OH)_2}} + K_2m_{\mathrm{OH^-}} + K_3m^2_{\mathrm{OH^-}}/\gamma^2_{\mathrm{MOH}}\ 1a/_{\mathrm{H_2O}} \quad (5)$$

where $\mathrm{M^+}$ represents a univalent cation. The principal assumption involved in this simplification is that of unit ratio for $\gamma_{\mathrm{OH^-}}/\gamma_{\mathrm{HHgO_2^-}}$, which appeared to be justifiable in the analogous cases of silver[2] and copper[3] oxides to ionic strengths of about unity.

The solubility data for both red and yellow oxides can be represented by straight lines up to nearly one molal alkali. No difference is observed in the solubilities of the yellow oxide in sodium, potassium or lithium hydroxide up to 0.5 *M* alkali. Because of the linearity in the solubility curve, the contribution of the third term in equation (5) to the solubility must be less than the experimental error up to 2 molal alkali; therefore, this term may be dropped from the equation. A theoretical justification for this procedure will be given later.

The solubility of red mercuric oxide may, therefore, be represented by the equation

$$S_{\mathrm{Hg(r)}} = m_{\mathrm{Hg(OH)_2}} + K_2m_{\mathrm{OH^-}} \quad (6)$$

and that of yellow mercuric oxide by

$$S_{\mathrm{Hg(y)}} = m_{\mathrm{Hg(OH)_2}} + K_2m_{\mathrm{OH^-}}\ a_{\mathrm{HgO(y)}} \quad (6^1)$$

K_2 is the slope of the curve when $S_{\mathrm{Hg(r)}}$ is plotted against molality of $\mathrm{OH^-}$ ion, and was determined to be 3.2×10^{-5} from a large scale plot of the data. The slope of the curve for yellow oxide was found to be 3.3×10^{-5}. Since $a_{\mathrm{HgO(y)}}$ is calculated in a later section to be 1.054, K_2 becomes 3.1×10^{-5}. The average of these two values, 3.15×10^{-5}, may be taken as the best value of K_2.

The Basic Dissociation Constant of Mercuric Hydroxide.—One striking fact is evident from an examination of the solubility curves in dilute alkali, namely, that there is no perceptible decrease from the solubility in pure water in either case. An examination of equation (1) reveals that this behavior is evidence of a very low basic dissociation constant for mercuric hydroxide. The solubility curves of silver[2] and copper[3] oxides and cadmium hydroxide[9] were found to possess pronounced minima, indicating substantially complete ionization. It is well known, however, that mercuric compounds possess unusually low degrees of dissociation.

Data in the literature support the observation of low basic dissociation. Hulett[8] found that on dissolving mercuric oxide in conductivity water no increase in conductivity could be observed. Schick[7] found that mercuric oxide did not in the least saponify ethyl acetate solution in thirty-seven hours. During this investigation the conductivities of a number of pure water samples of mercuric oxide were measured and found to be approximately 2.3×10^{-6} mho, which is about the magnitude we would expect for pure water shaken three weeks in glass containers.

By combining the water solubility of red oxide with its solubility product, as taken from the literature, a value for the basic dissociation constant of mercuric hydroxide may be obtained.

$$\mathrm{Hg(OH)_2} = \mathrm{Hg^{++}} + 2\mathrm{OH^-} \quad (7)$$

The solubility product of mercuric hydroxide is calculated to be 4×10^{-26} by Grossmann,[10] 1.5×10^{-26} by Fulda,[11] and 4×10^{-26} by Allmand[12] from the e. m. f. of mercuric oxide/alkali cells. Taking 4×10^{-26} as the best value

$$[\mathrm{Hg^{++}}][\mathrm{OH^-}]^2 = K_7[\mathrm{Hg(OH)_2}] = 4 \times 10^{-26}$$
$$K_7 = 1.8 \times 10^{-22}$$

The $\mathrm{OH^-}$ ion concentration furnished by the mercuric oxide in a saturated solution can be calculated from the value of the basic dissociation constant or from the solubility product. Such

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[9] Piater, *Z. anorg. allgem. Chem.*, **174**, 321 (1928); Johnston and Leland, Leland, Dissertation, Ohio State University, 1937.

[10] Grossmann, *Z. anorg. Chem.*, **43**, 368 (1905).

[11] Fulda, *Z. Elektrochem.*, **10**, 80 (1904).

[12] Allmand, *ibid.*, **16**, 254 (1910).

a calculation shows the value of the OH^- ion concentration to be 4×10^{-9} mole/liter which is considerably less than that supplied by the solvent. Assuming as a first approximation that all the hydroxyl ions are furnished by the first basic dissociation, the degree of dissociation becomes 0.002%.

The Dissociation Constants of Mercuric Acid.—The constant for the ionization of water may be written

$$K_w = (a_{H^+}\, a_{OH^-})/a_{H_2O}$$

We thus have for the first dissociation

$$H_2HgO_2 = H^+ + HHgO_2^- \qquad (8)$$

$$K_8 = \frac{a_{H^+}\, a_{HHgO_2^-}}{a_{H_2HgO_2}} = \frac{K_w a_{H_2O}\, m_{HHgO_2^-}}{a_{Hg(OH)_2}\, m_{OH^-}} = \frac{K_w m_{HHgO_2^-}}{m_{H_2HgO_2}\, m_{OH^-}}$$

The last simplification follows from the fact that in solutions as dilute as those used here the activity of water may be set equal to unity and the activity of the mercuric hydroxide to its molality. Taking the dissociation constant of water to be 1.01×10^{-14} at 25°,[13] and using the measured slopes and water solubilities for both forms, K_8 becomes 1.4×10^{-15} from the data for both red and yellow oxides.

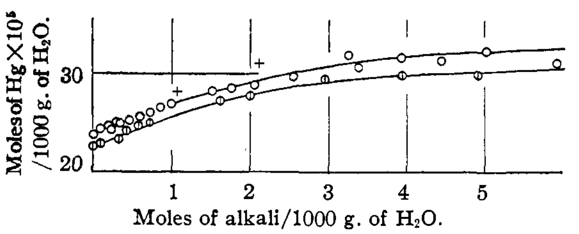

Fig. 3.—Solubility of red and yellow mercuric oxide in concentrated solutions of alkali: +, Fuseya; O, yellow oxide; ⦶, red oxide.

By assuming a reasonable value for the second dissociation constant of mercuric acid

$$HHgO_2^- = H^+ + HgO_2^{=} \qquad (9)$$

we may calculate a probable value for the third term in equation (5). The first and second dissociation constants of di- and tribasic acids of this approximate strength ordinarily differ by a factor of 10^3 to 10^4. Assuming $K_9 = 10^{-3}K_8$, and using the relationship[3] K_9 becomes 4.5×10^{-9}.

$$K_9 = K_w K_3/K_2$$

Employing Harned's data for the activity coefficients of sodium hydroxide,[14] we find that in 1 *M* sodium hydroxide the concentration of $HgO_2^=$ ion is only 0.0009×10^{-5} mole/1000 g. H_2O. This is less than experimental error; it explains the linearity observed, and justifies dropping the quadratic term from the equation as we have done. Conversely, this calculation makes it evident that we cannot hope to calculate even a rough value for K_9 from solubility data.

The Solubility of Yellow Mercuric Oxide in Alkaline Salt Solutions.—To determine the influence of added salts on the solubility of mercuric oxide in alkali, solubility determinations were made on samples in which the alkali concentration was held approximately constant, but the ionic strength was varied from 0.8 to 6.5 by the addition of sodium nitrate, potassium nitrate and sodium sulfate. Similar experiments on silver oxide[2] indicated that the solubility was nearly independent of salt concentration, which was confirmation of the assumption of unit ratio for $\gamma_{OH^-}/\gamma_{AgO^-}$. In the case of mercuric oxide, however, the solubility is increased considerably by the added salts, the solubility being a linear function of the salt concentration up to ionic strength of two or three. Scrutiny of Figs. 3 and 4 reveals that there is no relation between ionic strength and the solubility of mercuric oxide. This fact suggests that specific reactions are responsible for the solubility in the alkali and the alkaline salt solutions. We believe the linear dependence of solubility on salt concentration in the more dilute range is best explained by reactions of the type

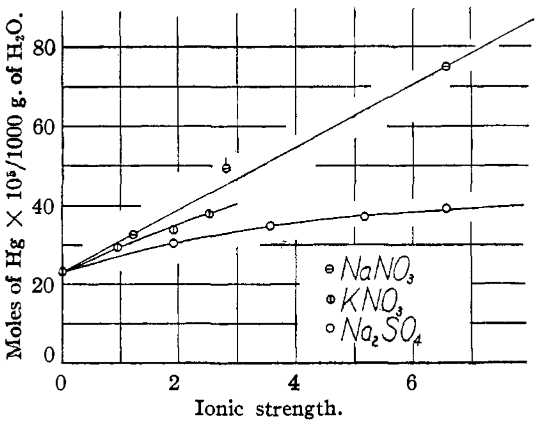

Fig. 4.—Solubility of yellow mercuric oxide in alkaline salt solutions (alkali is approx. 0.15 *N* NaOH): ⊖, $NaNO_3$; ⦶, KNO_3; ○, Na_2SO_4.

$$HgO + H_2O + NO_3^- = Hg(OH)_2(NO_3)^-$$
$$HgO + H_2O + SO_4^= = Hg(OH)_2(SO_4)^=$$

or, in other words, that basic salts are formed in solution. This view appears plausible when we

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(13) "International Critical Tables," Vol. VI, p. 152.

(14) Harned, This Journal, 47, 676 (1925).

consider the rather pronounced tendency of mercury to form such compounds.

It is apparent that the data in alkaline salt solutions, unfortunately, give no information concerning the ratio $\gamma_{OH^-}/\gamma_{HHgO_2^-}$.

Free Energy Calculations.—As it will be needed in later calculations, we will first obtain a revised value for the free energy of formation of hydroxyl ion. The most accurate value for the free energy of the reaction

$$H_2\ (g) + {}^1/{}_2O_2\ (g) = H_2O\ (l) \qquad (10)$$

is $\Delta F^\circ = -56{,}720$ cal., as determined by Giauque and Ashley[15] from spectroscopic data. Combining this value with other data given by Lewis and Randall,[16] we have

$$ {}^1/{}_2H_2\ (g) + {}^1/{}_2O_2\ (g) + e^- = OH^-; \quad \Delta F^\circ = -37{,}615 \text{ cal.} \qquad (11)$$

For the reaction

$$H_2O\ (l) + HgO_{(r)} = Hg(OH)_2(aq); \quad K_{12} = a_{Hg(OH)_2} \qquad (12)$$

we may set the activity of mercuric hydroxide equal to its molality. We then have $\Delta F^\circ = -RT \ln K_{12} = 4979$ cal.

The corresponding equation for yellow mercuric oxide is

$$H_2O\ (l) + HgO_{(y)} = Hg(OH)_2(aq); \quad K_{12} = \frac{a_{Hg(OH)_2}}{a_{HgO(y)}}$$

Since K_{12} must have the same value for both forms of oxide, $a_{HgO(y)} = 1.054$. Then from the equation $\Delta F = RT \ln a$, we obtain

$$HgO_{(r)} = HgO_{(y)}; \quad \Delta F = 31 \text{ cal.} \qquad (13)$$

The free energy of ionization of $Hg(OH)_2$ may be calculated from the ionization constant.

$$Hg(OH)_2 = Hg^{++} + 2OH^-; \quad \Delta F^\circ = 29{,}680 \text{ cal.} \qquad (14)$$

Combining equations (12) and (14)

$$HgO + H_2O = Hg^{++} + 2OH^-; \quad \Delta F^\circ = 34{,}660 \text{ cal.} \qquad (15)$$

From the solubility in alkali, the free energy of formation of bi-mercurate ion may be obtained.

$$HgO + OH^- = HHgO_2^-; \quad \Delta F^\circ = -RT \ln K_2 = 6145 \text{ cal.} \qquad (16)$$

The results already obtained, combined with the free energy of the reaction $Hg = Hg^{++}$, permit a calculation of the free energy of formation of mercuric oxide. The mercury–mercuric ion electrode potential has not been directly measured, but can be calculated from measured values of the mercury–mercurous ion and mercurous ion–mercuric ion standard potentials. The first of these may be taken as -0.7986 v.[16] (p. 419). The mercurous–mercuric standard potential is given as -0.9050 v. by Popoff and collaborators.[17]

Therefore, Hg/Hg^{++}, $E^\circ = {}^1/{}_2(-0.7986 - 0.9050) = -0.8518$ v. and

$$Hg\ (l) = Hg^{++} + 2e\Delta F^\circ = -2FE^\circ = 39{,}309 \text{ cal.} \qquad (17)$$

combining equations (10), (11), (15) and (17)

$$Hg\ (l) + {}^1/{}_2O_2\ (g) = HgO_{(r)}; \quad \Delta F^\circ = -13{,}861 \text{ cal.} \qquad (18)$$

The free energy of formation of mercuric oxide calculated by Lewis and Randall[16] (p. 484), when revised using the spectroscopic value for the free energy of formation of water, becomes $\Delta F^\circ = -13{,}968$ cal. The agreement between this value and the one calculated above is very good, which indicates that the dissociation constant of mercuric hydroxide, and the solubility of the oxide, which enter into the calculation, are substantially correct.

For yellow mercuric oxide we have

$$Hg\ (l) + {}^1/{}_2O_2\ (g) = HgO_{(y)}; \quad \Delta F = -13{,}830 \text{ cal.}$$

Combining (10), (12), and (18), and taking $-13{,}861$ cal. for the free energy of formation of mercuric oxide

$$H_2\ (g) + O_2\ (g) + Hg\ (l) = Hg(OH)_2\ (aq); \quad \Delta F^\circ = -65{,}602 \text{ cal.} \qquad (19)$$

Combining (11), (16), and (18)

$$Hg\ (l) + O_2\ (g) + {}^1/{}_2H_2(g) + e = HHgO_2^-; \quad \Delta F^\circ = -45{,}331 \text{ cal.} \qquad (20)$$

The Allotropy of the Oxides of Mercury.—The difference in free energy between red and yellow mercuric oxide has been calculated to be only 31 cal. or about 0.2% of ΔF of either form. This free energy difference is more accurate than could be obtained from calorimetric data. While this value is very small, nevertheless it cannot be cited as definite evidence for the identity of red and yellow oxides. However, the solubility data on the red and yellow forms of PbO, which are unquestionably allotropic, lead to a free energy difference of only 160 cal.[18] The samples of yellow oxide, however, were certainly more finely divided than those of the red variety. Microscopic measurements showed the yellow oxide to contain, for the most part, particles whose size ranged from 1–10μ while in the case of the red oxide the size ranged from 10–30μ. Some samples of precipitated yellow oxide contained no particles larger than 0.5μ. A sample of red oxide finely ground in an agate mortar was found to have a solubility about 5% greater than that of the

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[15] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[16] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, N. Y., 1923, p. 487.

[17] Popoff, *et al.*, THIS JOURNAL, **53**, 1195 (1931).

[18] Randall and Spencer, *ibid.*, **50**, 1572 (1928).

yellow oxide. The color, however, was much more red than the samples of the yellow oxide.

Further work is necessary before one can definitely attribute the free energy difference between the red and yellow forms to either difference in particle size, or to allotropy.

Summary

We have determined the solubility of red mercuric oxide in water, and in sodium hydroxide solutions, and of yellow mercuric oxide in water, and in sodium, potassium, lithium hydroxide solutions, and in alkaline salt solutions. These determinations have been made at 25 ± 0.01°.

The data indicate no minima in the solubility curves of red and yellow mercuric oxides in alkali solutions; in each case the solubility is a linear function of the alkali concentration up to approximately one normal alkali. The two curves are nearly parallel, the solubilities differing by about 5%.

The solubility curves in pure alkali establish the amphoteric nature of mercuric oxide by the constancy of the equilibrium constant, K_2

$$HgO + OH^- = HHgO_2^- \qquad (2)$$

A number of free energy calculations have been made with the aid of the solubility results. These include the ΔF of formation of mercuric oxide.

The first dissociation constant of mercuric acid has been evaluated from the data.

The dissociation constant of mercuric hydroxide as a base has been calculated, and found to be 1.8×10^{-22}, a fact which indicates an extraordinarily small degree of dissociation, namely, 0.002% in the saturated solution.

The data indicate that the difference in free energy between red and yellow mercuric oxide is only 31 cal./mole.

The data in alkaline salt solutions indicate that definite reactions are taking place between the oxide and the salts, probably the formation of basic salts. The data give no information concerning the ratio $\gamma_{OH^-}/\gamma_{HHgO_2^-}$.

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Organo-metallic Compounds of Indium[1]

BY WALTER C. SCHUMB AND H. IRVING CRANE

Of the elements in Group III of the Periodic Table which are known to form organo-metallic compounds, least attention appears to have been given to indium, due to the unavailability of this element until recent years, and to the ease of oxidation and of hydrolysis of its organo-metallic compounds.

Spencer and Wallace,[1a] studying the behavior of the aluminum group of metals with organic halides, found that indium reacted with iodobenzene and with α-bromonaphthalene, giving intermediate products, which were not isolated, but which gave benzene and naphthalene, respectively, on steam distillation. In 1910, Thiel and Kölsch[2] mentioned that they had worked with both the aliphatic and aromatic compounds of indium, but the subsequent complete paper has not appeared. They observed, however, that the alkyl compounds oxidized easily, the aryl compounds more sluggishly.

Goddard[3] refers to some otherwise unpublished work in which he prepared diphenylindium chloride and a basic phenylindium oxide. In 1934, Dennis[4] and his co-workers prepared trimethylindium and studied its physical properties, its oxidation and hydrolysis. In patents issued to Groll[5] mention is made of triethylindium, but no data are listed as to yields or properties.

The present paper is concerned chiefly with the preparation of triphenylindium, diphenylindium bromide and iodide, and of phenylindium dibromide and diiodide. A study of the properties of these substances indicates that in its organo-

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[1] Presented at the second annual symposium of the Division of Physical and Inorganic Chemistry, Cleveland, Ohio, Dec. 27–29, 1937.

[1a] J. F. Spencer and M. L. Wallace, *J. Chem. Soc.*, **93**, 1827 (1908).

[2] A. Thiel and H. Kölsch, *Z. anorg. allgem. Chem.*, **66**, 320 (1910).

[3] A. E. Goddard, editor, in J. N. Friend, "A Textbook of Inorganic Chemistry," Longmans, Green and Co., New York, 1928, Vol. XI, part 1, p. 235.

[4] L. M. Dennis, R. W. Work, E. G. Rochow and E. M. Chamot, THIS JOURNAL, **56**, 1047 (1934).

[5] H. P. A. Groll, U. S. Patents 1,938,179 and 1,938,180, Dec. 5, 1933.