rise in heat capacity of the solid form as the melting point is approached. We obtain from this empirical equation a value of 13.07 cal. per mole for 25°, and a mean value of 13.97 cal. per mole for the interval 25–100° in good agreement with the work already mentioned.

A straight line was found to fit the data for liquid iodine within experimental error. This gives then a constant molal heat capacity for liquid iodine of 19.5 ± 0.3 cal. per mole for the interval 113.6–160°. It will be recalled that Carpenter and Harle[3] found an initial value of 20.0 cal. per mole at the melting point, followed by a rapid decrease with increasing temperature. In this connection it should be mentioned that their work embraces only five runs on liquid iodine with individual deviations of over 3%. The method employed in this work is not suitable for investigating this trend of heat capacity. However, it would now appear certain that the values given by Favre and Silbermann,[4] Abegg and Halla,[5] and the "International Critical Tables" are quite erroneous.

The heat of fusion of iodine at the melting point is calculated to be 3740 ± 20 cal. per mole.

Acknowledgment.—The authors wish to express their appreciation of the assistance given them by Mr. Austin L. Wahrhaftig in the calibration of the apparatus and in the preparation of the iodine capsules.

Summary

Employing the method of mixtures, the heat of fusion of iodine at the melting point was found to be 3740 ± 20 cal. per mole. The molal heat capacity of solid iodine in the limited temperature interval 25–113.6° can be expressed within ±0.5% of the measured values by the equation $c_p = 13.07 + 3.21 \times 10^{-4}(t-25)^2$. For liquid iodine from the melting point up to 160°, the molal heat capacity is 19.5 ± 0.3 cal.

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

The Solubility of Gold Hydroxide in Alkali and Equilibria in the Saturated Solutions[1]

BY HERRICK L. JOHNSTON AND HOLLIS L. LELAND[2]

The extent of acid character associated with the hydroxides of the silver sub-group elements, as measured by solubility of the oxide or hydroxide in alkali, forms an interesting study because of the regular increase in air-stable valence from silver to gold. Quantitative data on the equilibria present in alkaline solutions of silver and of di-valent copper have been presented in earlier papers.[3] This paper presents similar data for trivalent gold. The results show the expected dependence on the valence of the metal, and establish quantitatively the correctness of the explanation we have assigned previously to solutions of this character.

Experimental

Apparatus and procedure were similar to those employed in the earlier work from this Laboratory except for such changes as were necessary to adapt the procedure to gold.

Auric hydroxide was prepared out of contact with air, by the method of Roseveare and Buehrer,[4] in the preparation train described by Johnston, Cuta and Garrett.[3] Gold was precipitated from a boiling aqua regia solution of gold by the dropwise addition of three normal potassium hydroxide; the mother liquor was siphoned off and the precipitate dissolved in the minimum amount of boiling three normal potassium hydroxide; and, finally, the gold was again precipitated by dropwise addition of sulfuric acid until the solution was just acid to litmus. This product was boiled for an hour;[4] washed twice with conductivity water; and transferred under nitrogen to a special wash flask[3] where it received fifteen additional washings with conductivity water. Qualitative tests for sulfate and chloride ions, made after the tenth washing, were invariably negative. The product was then stored under conductivity water and nitrogen until ready for use. Six separate lots of auric hydroxide were prepared in this manner to furnish the samples needed in this investigation. The data from the six lots are indistinguishable.

The product prepared in the above manner was reddish-brown in color and was composed of agglomerates of small biaxial crystals.[5] The crystalline character was estab-

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(1) Presented before the Division of Physical and Inorganic Chemistry of The American Chemical Society, at its Rochester meeting, September, 1937.

(2) Present address: Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J.

(3) (a) H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933); (b) L. A. McDowell and H. L. Johnston, *ibid.*, **58**, 2009 (1936).

(4) Roseveare and Buehrer, *ibid.*, **49**, 1989 (1927).

(5) Precipitation from *hot*, *strongly basic* solutions was found to yield a dense, black product whose properties differ markedly from

lished by viewing some of the precipitate between crossed Nicols in a petrographic microscope. Oil immersion and a magnification of twelve hundred diameters were necessary.

The composition of the crystals was established by their weight loss in hydrogen at 500° and, independently, by quantitative estimation of gold in hydrochloric acid solutions of weighed samples. Six determinations on samples which were desiccated over calcium chloride for a week gave an average gold analysis of 78.5%, with an average deviation from the mean of only 0.3%. A sample which was given an additional drying in air at 105° for fifteen minutes, analyzed 79.5% gold. These figures identify the brown product as $Au(OH)_3$ (stoichiometric composition, 79.45% gold). This is easily distinguished from the oxide (Au_2O_3, composition, 89.15% gold).[6]

Gold for the preparation of auric hydroxide was precipitated from an aqueous solution of c. p. gold chloride through reduction with oxalic acid. The resulting sponge was macerated and washed thoroughly, was digested in hot concentrated sulfuric acid and again washed, was converted back to the chloride and the fore-described process repeated, and was finally dried and fused in an alundum crucible.

Solutions of **sodium hydroxide** and of **potassium hydroxide** were prepared from pure amalgams in the manner described in earlier papers,[3] or by the treatment of the concentrated alkali with just sufficient barium hydroxide to remove carbonate.

All **salts**, with the exception of ferrous sulfate, were twice-recrystallized "reagent quality" chemicals. The **ferrous sulfate** was a reagent quality product used without recrystallization. **Acids** employed were c. p. reagents.

Conductivity water, with a conductivity which never exceeded 2×10^{-6} mho, was used exclusively both in the preparation of solutions and in purification steps.

Analytical Procedure

The alkali content of the solutions was determined by titration with standard sulfuric acid to the first sharp color change with methyl orange. When significant, corrections were applied for the indicator end-point and for the acid required to convert aurate ions to the hydroxide.

Gold was determined by potentiometric titration. We made preliminary studies of the use of potassium iodide,[7] stannous chloride,[8] potassium ferrocyanide, potassium thiocyanate and potassium cyanide as possible reagents for the titration, but found that these were either too insensitive or their end-points too erratic for satisfactory results in very dilute solutions of gold. With ferrous sulfate[9] as reagent and a technique similar to that previously described[3] we obtained a high sensitivity and good accuracy. Accordingly we adopted this reagent for the analysis. Titrations were carried out in a 250-cc. beaker connected by an agar–agar salt bridge to a calomel half cell. A platinum foil, cleaned with pumice before each titration, served as the indicator electrode. The standard ferrous sulfate solution (0.0003 *M*) was added from a microburet and the titration carried out in an atmosphere of nitrogen. It was found that the addition of two drops of 0.5 *M* hydrochloric acid and two drops of methyl orange indicator to the neutral gold solution (100–125 cc.) increased the sensitivity of the titration. In cases where the original alkalinity of the aurate solution had been less than 0.3 *M*, solid potassium chloride was added to the cell to reduce its resistance. The cell came to equilibrium quickly after each addition of the ferrous sulfate. The change of potential at the end-point was usually between 5 and 10 mv. for the addition of 0.02 cc. of the standard reagent.

The ultimate standard for the determination of gold was an approximately 0.06 *M* solution of gold chloride which was prepared from a weighed quantity of pure gold. The ferrous sulfate, which was stored under nitrogen, was standardized frequently against this standard gold solution under conditions closely identical with those employed in the analysis of samples. Over a period of nine weeks, during which time most of the data were obtained, the ferrous sulfate standard remained constant to within 0.5%.

The Data

Equilibrium was approached both from the side of supersaturation and that of undersaturation. Supersaturation was produced by four days of agitation in a 40° bath, after which the flasks were transferred to the 25 (±0.01°) thermostat for a final period of agitation. A preliminary investigation revealed that a week to ten days in the 25° thermostat was ample time to bring the supersaturated solutions to equilibrium. The usual time given was about two weeks.

Somewhat more time was required to reach equilibrium from the side of undersaturation. Table I presents some data obtained as a function of the time of shaking. The flasks were opened and sampled after ten and twenty days of agitation and were then resealed, and shaking resumed.

TABLE I

RATE OF SOLUTION OF AURIC HYDROXIDE IN 0.300 *M* SODIUM HYDROXIDE, BY AGITATION AT 25°

Shaking period, days	Concentration of gold in the filtrate (moles/1000 g. of water × 10^4)		
	Lot VIII	Lot IX	Lot X
10	1.6	4.1	4.6
20	5.3	5.6	5.4
32	5.4	5.5	5.6

The rate of solution was determined on three of the six lots of brown crystals which are referred to in an earlier paragraph. The particle size was less for Lots IX and X than for VIII. Table I refers to solution in 0.3 *M* sodium hydroxide but results obtained at other alkalinities, including ones above 0.4 *M*, permit the same conclusions. Ac-

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those of the brown precipitate. Efforts were unsuccessful to dissolve a detectable amount of the black precipitate even after two to four weeks of agitation in various concentrations of alkali between 0.01 and 6 *M*. Two hours of boiling in 0.4 *M* sodium hydroxide likewise failed to give a test for gold in the filtrate. This sluggishness toward solution is accompanied by an equally remarkable inertness toward reduction, since hydrogen at 500° produced no reaction in two hours.

(6) In a further experiment dry nitrogen was passed over a sample of the hydroxide at 150°, and the moisture collected and weighed in a calcium chloride drying tube. It was found that under these conditions the hydroxide decomposes quantitatively to the oxide and that the latter does not sensibly decompose.

(7) Someya, *Sci. Reports Tohôku Univ.*, **19**, 124 (1930); Someya, *Z. anorg. allgem. Chem.*, **187**, 357 (1930).

(8) Müller and Bennewitz, *ibid.*, **179**, 113 (1929); Müller and Stein, *Z. Elektrochem.*, **36**, 376 (1930); Müller and Görne, *Z. anal. Chem.*, **73**, 385 (1928).

(9) Müller and Weisbrod, *Z. anorg. allgem. Chem.*, **156**, 17 (1926); Müller and Weisbrod, *ibid.*, **169**, 394 (1928).

cordingly we adopted three weeks as the minimum shaking period for approach to equilibrium from the side of undersaturation. Most samples were agitated somewhat longer.

When the shaking period was ended the samples were sedimented in another 25° thermostat for from two to ten days, before analysis. Flasks which showed a noticeable Tyndall beam after this sedimentation were discarded. We had little trouble in this respect, with auric hydroxide prepared in the manner described, except in the region of low alkalinity. We found it impracticable to obtain data at alkalinities below 0.07 *M* because of the almost invariable presence of colloids at these dilutions. This corresponds to the experience with copper.[3b]

Following sedimentation, a portion of the clear solution was removed by careful decantation, passed through a filter of sintered Jena glass, and analyzed by the methods which have been described. The first few cubic centimeters of solution that passed through the filter was discarded.

TABLE II

SOLUBILITY OF AURIC HYDROXIDE IN AQUEOUS SODIUM HYDROXIDE, AT 25°

Moles of NaOH per 1000 g. H_2O	Moles of gold per 1000 g. $H_2O \times 10^4$	
	Undersaturated	Supersaturated
0.0683	....	0.73
.0752	0.89	.85
.0939	.97	1.00
.0968	....	1.51
.1005	1.01	1.00
.1100	1.13	1.09
.1507	2.01	2.00
.1678	....	2.13
.1696	2.33	2.31
.1998	2.91	....
.2364	....	4.44
.2595	4.49	4.50
.2997	5.49	5.79
.3254	....	6.53
.3547	7.99	7.98
.3778	9.05	9.02
.3900	....	9.73
.4138	....	10.54
.4215	....	9.79
.4402	9.44	....
.4941	7.70	7.77
.519	....	7.14
.522	7.33	7.20
.543	7.60	6.34
.660	....	4.90
.667	4.62	4.69
.748	3.46	3.53
.790	3.23	3.17
.840	2.61	2.63
1.048	1.47	1.44
1.049	1.50	1.48
1.299	1.60	....
1.445	....	1.94
1.682	1.69	1.70
2.293	2.01	2.01
2.845	2.22	2.20
3.095	2.39	2.32
3.541	2.61	2.62
3.983	2.68	2.63
6.05	3.76	3.84
8.37	5.32	5.23

Table II records the solubility data obtained in pure aqueous sodium hydroxide, with samples from undersaturation and from supersaturation recorded separately.[10]

Blanks in the table represent cases in which either: (1) the undersaturation member in early experiments was not shaken the requisite three weeks; (2) colloidal material was observed; or (3) a sample was lost in handling.

Table III contains data we obtained on the solubility in pure conductivity water.

TABLE III

THE SOLUBILITY OF AURIC HYDROXIDE IN PURE WATER (MOLES OF GOLD/1000 G. OF WATER)

Undersaturation	Supersaturation
0.034×10^{-4}	0.032×10^{-4}
.028	.037
.026	.030

Average 0.031×10^{-4}

Discussion and Interpretation of Results

The data of the preceding tables are shown graphically in Fig. 1, with black circles used to plot average values of sample pairs.

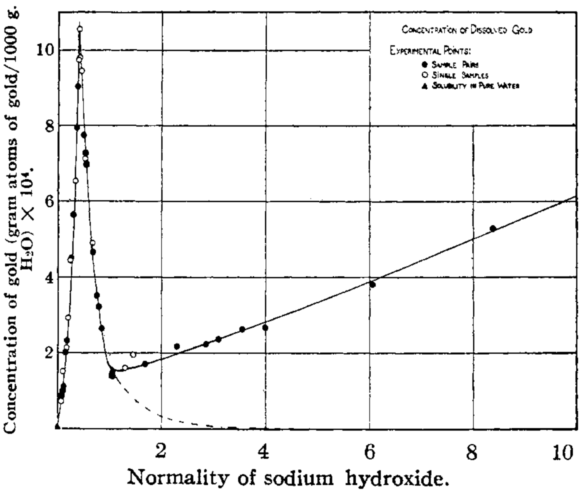

Fig. 1.—Solubility of gold hydroxide in sodium hydroxide solutions. The broken curve is the extrapolation of Eq. 6 above 1 *N* alkali.

The most noticeable feature of the graph is the sharp maximum at about 0.42 *M* sodium hydroxide. This is the result of a change in solid phase, revealed both by chemical analyses and by microscopic examination of solid residues re-

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[10] Alkalinities were determined separately for each sample. When significant differences were found for the two samples constituting a pair the data were corrected to a common alkalinity.

moved from equilibrated solutions. To the left of the maximum the equilibrium solid is identical with the initial brown hydroxide; to the right it is composed of greenish, needle-shaped crystals with a composition corresponding to the formula Na_2HAuO_3.[11] This behavior is analogous to that observed for cupric oxide[12] which exhibits a maximum solubility at about 15 N sodium hydroxide (volume normality) accompanied by a change in solid phase, identified as conversion from CuO to Na_2CuO_2.

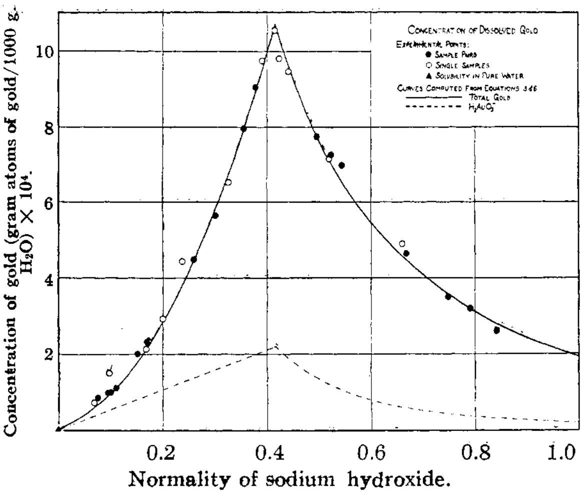

Fig. 2.—Solubility of gold hydroxide in sodium hydroxide.

We are able to fit the experimental curve to the left of the maximum, quantitatively, in terms of the reactions

$$Au(OH)_3 + OH^- = H_2AuO_3^- + H_2O \qquad (1)$$
$$Au(OH)_3 + 2OH^- = HAuO_3^= + 2H_2O \qquad (2)$$

with their corresponding equilibrium constants

$$K_1 = (m_{H_2AuO_3^-}/m_{OH^-})(\gamma_{H_2AuO_3^-}/\gamma_{OH^-})a_{H_2O} \qquad (1a)$$
$$K_2 = (m_{HAuO_3^=}/m^2_{OH^-})(\gamma_{HAuO_3^=}/\gamma^2_{OH^-})a^2_{H_2O} \qquad (2a)$$

The total solubility of gold, in equilibrium with $Au(OH)_3$ as the solid phase, is thus given by the relationship[13]

$$S_{Au} = m_{Au(OH)_3} + K_1 m_{NaOH}(p^\circ/p) + K_2 m^2_{NaOH}(1/\gamma_{NaOH})(p^\circ/p)^2 \qquad (3)$$

where m_{NaOH} refers to the stoichiometric molality; γ_{NaOH} is the mean activity coefficient of sodium hydroxide in the solution involved;[14] $(p^0 - p)$ is the vapor pressure lowering of water[15] and $m_{Au(OH)_3}$ represents a possible small solubility of undissociated gold hydroxide, whose contribution proves too small to possess significance in the present experimental fit.[16] The *continuous* curve to the left of the maximum in Fig. 2 is computed from equation (3) with the constants K_1 and K_2 set equal to 5.25 × 10^{-4} and 23.0 × 10^{-4}, respectively. The broken curve represents the concentration of $H_2AuO_3^-$ ion alone.

Explanation of the observed data to the right of the maximum requires the inclusion of the additional equilibrium

$$Na_2HAuO_3 = 2Na^+ + HAuO_3^= \qquad (4)$$

with its attendant constant

$$K_4 = (m^2_{Na^+}\ m_{HAuO_3^=})(\gamma^2_{Na^+}\ \gamma_{HAuO_3^=}) \qquad (4a)$$

It may be shown simply, from equations (1a), (2a) and (4a), that in the presence of either solid phase the relative concentration of the di-hydrogen and mono-hydrogen ions must conform to the relationship

$$(m_{H_2AuO_3^-}/m_{HAuO_2^=}) = (K_1/K_2)(a_{H_2O}/m_{NaOH})(\gamma_{HAuO_3^=}/\gamma_{H_3AuO_3^-}\ \gamma_{OH^-}) \qquad (5)$$

With the use of equations (4a) and (5) and the introduction of the same simplifying limiting relationships used in deriving equation (3)[3b] the solubility of Na_2HAuO_3 is given by the expression

$$S_{Au} = m_{Au(OH)_3} + (K_4K_1/K_2)(1/m^3_{NaOH})(p/p^\circ)(1/\gamma^4_{NaOH}) + K_4\ (1/m^2_{NaOH})(1/\gamma^6_{NaOH}) \qquad (6)$$

The last two terms of this equation represent saturation values of $H_2AuO_3^-$ and $HAuO_3^=$ ions, respectively.

The solid curve to the right of the maximum in Fig. 2 is calculated from equation (6) with K_4 set equal to 1.53 × 10^{-5} and the other constants given the values previously determined for equa-

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[11] Conversion to this formula was complete only after several weeks of agitation at 25°. This results from the protective action of an initial coating of the insoluble salt. The samples which were analyzed to establish the formula were shaken in 1 M sodium hydroxide until they showed only microscopic traces of the initial brown hydroxide. They were then rinsed with ether, dried in air at 25° and analyzed for gold and for combined water—the latter by weight loss in air at 140°. Two gold determinations yielded 68.3 and 69.8%, respectively, and combined water analyzed approximately 4%. These figures correspond to the formula Na_2HAuO_3 (67.6% gold, 3.1% water) but not with the formulas NaH_2AuO_3 (72.6% gold, 6.6% water) or $NaAuO_2 \cdot 2H_2O$ (68.4% gold, 12.4% water). The latter formula was assigned by Meyer [*Compt. rend.*, **145**, 805 (1907)] to the "greenish, acicular crystals" formed in strong sodium aurate solution. Our assignment of the formula Na_2HAuO_3 is also confirmed by the nature of the solubility curve to the right of the solubility maximum (*cf. seq.*).

[12] E. Müller, *Z. physik. Chem.*, **105**, 73 (1923).

[13] *Cf.* eq. (3) and (4) of ref. 3b.

[14] For the computations we employed the activity coefficients tabulated by Harned [THIS JOURNAL, **47**, 676 (1925)] for pure sodium hydroxide solutions.

[15] Taken from the "International Critical Tables," Vol. III, p. 373, for sodium hydroxide solutions.

[16] $m_{Au(OH)_3}$ was taken as constant at 3 × 10^{-6} mole per 1000 g. of water in the computation by equations (3) and (6). This value, which is the total observed solubility in pure water, is of course an upper limit and is probably somewhat too high since we believe that there is some ionization in the saturated aqueous solution. For the purpose of testing equations (3) or (6), or determining their constants, $m_{Au(OH)_3}$ may be varied between 3 × 10^{-6} and zero without appreciable significance in the result.

tion (3) in dilute alkali. The fit is good up to about 1 *M* sodium hydroxide.[17]

As a further test of the relationship expressed in (3), and of the constants assigned, we measured the solubility of gold hydroxide in potassium sulfate solutions, with a fixed concentration of sodium hydroxide (0.2 *M*). With silver oxide the solubility in alkali was independent of the presence of salt.[3] For auric hydroxide, if our explanation is correct, there should be a dependence which enters through the inverse square of the activity coefficient of sodium hydroxide.[18] The results of this test are given in Table IV, which includes solubilities calculated[19] by equation (3). The agreement is good except for the point of highest salt concentration. This is near the solubility product limit for Na_2HAuO_3 and may exceed that for the potassium salt.

TABLE IV

SOLUBILITY OF AURIC HYDROXIDE IN ALKALINE SOLUTIONS (0.2 *M* NaOH) OF POTASSIUM SULFATE

Salt concn., *N*	Ionic strength	γ_{MOH}	Soly. calcd.	(moles/liter × 10^4) obsd.	
0.00	0.2	0.723	2.87	2.91	
.20	.5	.670	3.19	3.27	3.30
.54	1.0	.635	3.48	3.42	3.44
.87	1.5	.602	3.77	3.47	3.43

It seems necessary to assume the formation of AuO_3^{---} ions in solutions of base stronger than one normal, in order to account for the nearly linear rise in the solubility curve beyond 1 *M* sodium hydroxide. Equation (6), which accounts for $H_2AuO_3^-$ and $HAuO_3^{--}$ ions, leads to a rapidly descending solubility curve which deviates by a large factor from the observed data in strong alkali (*cf.* Fig. 1). While we would not expect this limiting equation, which includes assumptions as to the equality of activity coefficients of OH^- and $H_2AuO_3^-$ ions, to hold accurately in concentrated solution, neither does it appear reasonable that the assumptions can be in error by the factor implied in the observed discrepancy, especially in view of the reasonably good fits obtained even above one normal base for silver and for copper. Introduction of AuO_3^{---} ions by the reaction

$$Na_2HAuO_3 + OH^- = 2Na^+ + AuO_3^{---} + H_2O \quad (7)$$

appears to be the only reasonable alternative. If the simple mass action principle were applicable even this equilibrium would yield a descending solubility curve with increase in the concentration of base. However, the descent would be gradual; and introduction of the necessary activity coefficients would have the effect of increasing the calculated AuO_3^{---} ion concentration by several fold and could, in reason, account for the magnitude and slope of the observed data. However, we cannot make this treatment quantitative for alkalinities in which the calculation would be of interest. This explanation is entirely consistent with the acceptance of negligible concentration of AuO_3^{---} below about one normal base (*cf. seq.*).

Acid Dissociation Constants.—The *second* dissociation constant of auric acid, which corresponds to the step

$$H_2AuO_3^- = HAuO_3^= + H^+ \quad (8)$$

is computed readily from the constants K_1 and K_2 and the dissociation constant for water by the relationship

$$K_8 = K_w(K_2/K_1) = 4.4 \times 10^{-14} \quad (9)$$

with K_w taken to be 1.01×10^{-14} at 25°.

The *first* dissociation constant, which corresponds to the step

$$H_3AuO_3 = H_2AuO_3^- + H^+ \quad (10)$$

is given by the relationship

$$K_{10} = K_w(K_1/m_{Au(OH)_3}) \quad (11)$$

We are only able to set an upper limit to $m_{Au(OH)_3}$, namely, 3×10^{-6} based on the measured solubility in pure water. This results in a value of 1.8×10^{-12} as the *lower* limit for the first dissociation constant of the acid. We believe (*cf. seq.*) that the water solubility includes some contribution from $H_2AuO_3^-$ ions, which would make $m_{Au(OH)_3}$ *lower* than 3×10^{-6}, and K_{10} correspondingly *larger* than 1.8×10^{-12}. In either event the ratio between the first and second dissociation constants here deduced is of the order of magnitude commonly observed in acids of this approximate strength. The value of K_{10} places the strength of the *first* dissociation step of auric

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(17) That this fit is significant in the interpretation of the solution process, and not made possible by the arbitrary choice of an additional constant, is made evident through inability to fit the data with assumed equilibria other than that in (4).

(18) There is also a smaller influence, entering through the variation in the activity of water.

(19) The activity coefficient of the base, written as γ_{MOH}, was taken as the linear average of log γ_{NaOH} in Na_2SO_4 solutions and of log γ_{KOH} in K_2SO_4 solutions, with K and Na weighted in stoichiometric proportion. The activity coefficients of NaOH and of KOH in their respective sulfate solutions were obtained from the data of Harned and Åkerlöf [*Physik. Z.*, **27**, 411 (1926)] by extrapolation to 0.2 *M* solutions of base. The extrapolations were made with the aid of their equation (42) by setting the first two terms of that equation equal to empirical constants for a fixed ionic strength and a given base, and evaluating these with the aid of smooth curves drawn through the experimental γ's. This method of extrapolation was employed, rather than the full use of equation (42), since their equation deviates consistently from the experimental γ's in 0.01 *M* potassium hydroxide.

acid somewhat above that of the *third* step in the ionization of orthophosphoric acid.

An *upper limit* for the third dissociation constant can be calculated on the basis of measured solubilities. This calculation is based on the respective relationships

$$K = (K_w/K_3)m_{\text{NaOH}}\gamma^{10}_{\text{NaOH}}m_{\text{AuO}_3^{---}} \qquad (12)$$

$$K = (K_w/K_2)(\gamma^{6}_{\text{NaOH}}/m^{3}_{\text{NaOH}})m_{\text{AuO}_3^{---}} \qquad (13)$$

for equilibria with Na_2HAuO_3 or $Au(OH)_3$, respectively. Obviously $m_{\text{AuO}_3^{---}}$ for insertion in (12) cannot exceed the *total* solubility. Insertion of the *total* solubility in 1 *M* sodium hydroxide yields the value $K = 2 \times 10^{-15}$. Likewise insertion in (13) of a reasonable upper limit for the concentration of AuO_3^{---} ion in 0.4 *M* sodium hydroxide yields K equal to about 5×10^{-16}. We conclude that this third dissociation cannot much exceed 1×10^{-16}. A constant of this magnitude is consistent with the quantitative treatment which treats $m_{\text{AuO}_3^{---}}$ as negligible below 1 *N* alkalinity; is of the correct order of magnitude to account for the experimental curve in the region of high concentration of base and bears a reasonable ratio to the second dissociation constant K_3.

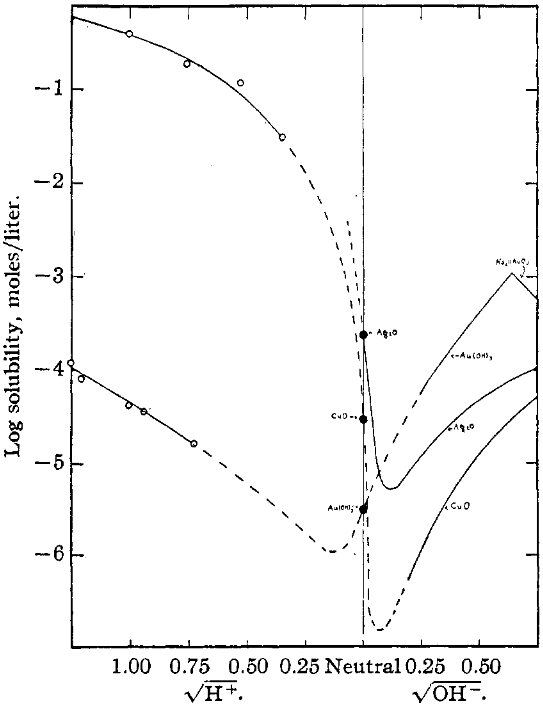

Fig. 3.—Solubility of the oxides (or hydroxides) of the first sub-group elements in acid: ○, experimental points in acid; ●, in water; ——, experimental curves; – – –, interpolated and extrapolated curves.

Comparison of the Acid Strengths and Amphoteric Properties of the Hydroxides of the Elements of Sub-Group I.—Table V brings together the acid dissociation constants of the elements of Sub-Group I, as determined in our several investigations. The lower limits for the first acid dissociation constants of copper[20] and of gold hydroxides, and the upper limit for the third dissociation constant for gold are included to permit the intercomparison of constants.

TABLE V

ACID DISSOCIATION CONSTANTS OF THE HYDROXIDES OF COPPER, SILVER AND GOLD IN THEIR AIR-STABLE VALENCES

	K_1	K_2	K_3
AgOH	7.9×10^{-13}	...	...
$Cu(OH)_2$	$>1.5 \times 10^{-13}$	7.9×10^{-14}	...
$Au(OH)_3$	$>1.8 \times 10^{-12}$	4.4×10^{-14}	$<5 \times 10^{-16}$

Figure 3 illustrates yet more clearly the relative behavior of these elements in both basic and acid solutions. The curves in acid solution are constructed from the data of Jaeger[21] for the solubility of cupric oxide in aqueous hydrofluoric acid, and of Jirsa and Jelinek[22] for the solubility of auric hydroxide in sulfuric acid of moderate concentrations. To permit the behavior of the three elements to show clearly on a common diagram solubilities are plotted on a logarithmic scale against the square roots of acid and of base normality. Broken curves are used for interpolation in those concentration regions to which the experimental measurements did not extend. Because of the square root scale along the abscissa these appear on a disproportionate scale on the alkaline side.

Only for silver has it been possible to follow the curve, experimentally, through the minimum. But for gold the low measured solubility in water and the course of the curve in sulfuric acid (which dissolves less gold at 0.5 *N* concentration than does sodium hydroxide at 0.07 *N* concentration) clearly places the minimum on the acid side of neutral.[23] This is interesting for it establishes

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[20] The *lower limit* for the first acid dissociation constant of cupric hydroxide, not included in reference 3e, is computed by setting $m_{\text{Cu(OH)}_2}$ equal to 7×10^{-7} mole/liter, the lowest measured solubility. The true $m_{\text{Cu(OH)}_2}$ is unquestionably lower than this and the true K_1 correspondingly higher than the value in the table—probably by one or more powers of ten.

[21] Jaeger, *Z. anorg. Chem.*, **27**, 22 (1901). Additional measurements in the presence of potassium fluoride and in nitric acid provided evidence that the solubility in hydrofluoric acid is due to action of hydrogen ions alone, and that no fluoride complex is formed.

[22] Jirsa and Jelinek, *Z. Elektrochem.*, **30**, 286 (1924).

[23] Mercuric oxide, recently investigated by Garrett and Hirschler [THIS JOURNAL, **60**, 299 (1938)], probably behaves in a similar manner.

auric hydroxide as predominantly acid even in its aqueous solution. The presence of a minimum on the alkaline side of neutral is clearly indicated for copper but its position and its depth are subject to some uncertainty. The construction shown, which places the copper minimum at a somewhat lower concentration of base than that at which the minimum occurs for silver, is in best agreement with observations in dilute alkali and with the observations in acid.

It is observed, from Table V and from Fig. 3, that: (1) the constants representing successive steps in the dissociation of copper hydroxide or of gold hydroxide bear ratios of 10^2, or greater; (2) that the first dissociation constants appear to increase in the order of increasing valence; (3) that the minima in the solubility curves move toward the acid side with increasing valence; (4) that the relative slopes of solubility curves on the basic side increase in the order silver, copper, gold; and (5) that they appear to follow just the opposite order on the acid side.

These observations are all consistent with the explanation by which we have accounted quantitatively for the solubilities of the individual oxides—namely, by the stepwise neutralization of weak acidic hydroxides in alkaline solution. They show, moreover, the predominant influence of valence in determining the acid strength of the hydroxide analogous to the well-known relationship found among different valence states of such distinct acids as H_2SO_4, H_2SO_3, HNO_3, HNO_2, etc. On the basis of ion size we would expect the acid strength to increase in the order gold, silver and copper for comparison at a common valence. We hope eventually to test this by comparison of the solubility curves of Ag_2O and of Cu_2O. Efforts to make the comparison with Au_2O were unsuccessful due to the instability of the lower oxide, in confirmation of the observation of other investigators.

The explanation which we have advanced for the solubility relations in alkaline solutions of oxides and hydroxides of the elements of Sub-Group I, and which we believe to be well confirmed by the quantitative treatment we have given, is also well supported by quantitative data on the solubility of cadmium hydroxide in dilute alkali. We expect to publish this in an early paper and will discuss in that paper the relationship of our data to the complex ion explanation of the solubility of metal hydroxides in alkali.

Summary

The solubility of auric hydroxide has been measured in pure water and in sodium hydroxide solutions to a concentration of eight normal. The solubility curve rises continuously from the value 3×10^{-6} mole of gold per 1000 grams of water to a maximum of about 1×10^{-3} mole per 1000 grams of water at about 0.42 *N* sodium hydroxide, falls steeply to a minimum solubility at about 1 *N* base and rises nearly linearly with higher concentrations of base.

The stable solid phase below 0.42 *N* sodium hydroxide has the composition $Au(OH)_3$ and, above 0.42 *N* sodium hydroxide, the composition Na_2HAuO_3.

The data are well accounted for, to the minimum at 1 *N* alkali, by the equilibria

$$Au(OH)_3 + OH^- = H_2AuO_3^- + H_2O$$
$$Au(OH)_3 + 2OH^- = HAuO_3^{--} + 2H_2O$$
$$Na_2HAuO_3 = 2Na^+ + HAuO_3^{--}$$

with account taken of the activity coefficient of sodium hydroxide in the solutions. This interpretation is confirmed by measurements in alkaline solutions of potassium sulfate.

It appears necessary to introduce the equilibrium

$$Na_2HAuO_3 + OH^- = 2Na^+ + AuO_3^{---} + H_2O$$

to account qualitatively for the observed rise in the solubility above 1 *N* sodium hydroxide.

Acid dissociation constants for the tribasic auric acid are computed from the data.

Our own data in basic solution and in pure water, in conjunction with data of Jirsa and Jellinek for the solubility of gold hydroxide in sulfuric acid, indicate that the expected minimum in the solubility curve will lie in dilute acid and that auric hydroxide is acidic, rather than basic, in pure water.

Solubility curves and acid dissociation constants are compared for the oxides and hydroxides of copper, silver and gold. The relative acid strengths of the hydroxides follow in the order gold, copper and silver and are consistent with the quantitative explanation of the solubilities as stepwise neutralization equilibria.

A sensitive potentiometric method for the quantitative determination of gold is described.

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