

TABLE V
 VAPOR PRESSURE OF BUTADIENE

T_c	$T_{abs.}$	$P_{exp.}$	$P_{calcd.}$	Diff. in mm.
-75.5	197.6	14.6	16.1	-1.5
63.4	209.7	35.4	37.4	-2.0
51.6	221.5	77.1	77.8	-0.7
39.4	233.7	153.4	153.7	-0.3
38.6	234.5	161.7	160.5	+1.2
32.7	240.4	219.0	216.6	+2.4
26.1	247.0	301.4	298.3	+3.1
19.9	253.1	400.5	397.8	+2.7
15.5	257.6	484.2	482.6	+1.6
10.4	262.7	599.9	599.1	+0.8
5.6	267.5	729.7	731.0	-1.3
- 1.5	271.6	854.0	859.1	-4.9

Summary

The number of molecules of vinylacetylene and butadiene condensing per alpha particle from radon is found to be 10.8 and 9, respectively. The $(\Delta(H_2 + CH_4))/-\Delta HC$ for these hydrocarbons is very low—practically the same as acetylene.

The predicted value of the $-M/N$ value for vinylacetylene agrees with the experimental value but there is no correspondence in the case of butadiene.

The vapor pressure of butadiene has been determined at a number of temperatures and the data have been fitted to a linear equation.

The boiling point is found to be -4.6° .

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The Solubility of Silver Oxide in Water, in Alkali and in Alkaline Salt Solutions. The Amphoteric Character of Silver Hydroxide

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This investigation had its inception in the effort to throw possible light on the uncertain behavior of the silver-silver oxide electrode in contact with alkali. Buehrer,² in an extensive investigation of cells which contained this electrode, found that the cells did not possess satisfactory reproducibility. Among the causes which may have contributed to this, Buehrer suggested the extremely low solubility of the oxide in contact with alkali. Some support was given to this suggestion by the fact that, with barium hydroxide as electrolyte, the measurements were somewhat more

(1) Assistant on the Chemical Faculty of the Technical University in Prague, Czechoslovakia, International Exchange Fellow, 1930-1931.

(2) Buehrer, Ph.D. Thesis, The University of California, 1921.

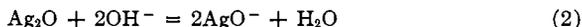
self-consistent than with potassium hydroxide and the statement, accredited to Berzelius, that "silver oxide is soluble in barium hydroxide but not in potassium hydroxide."

The project appeared the more interesting since it offered the opportunity to determine the possible amphoteric character of silver hydroxide. Although chemists are accustomed to regard as amphoteric a rather narrow group of hydroxides, of which those of aluminum, of antimony and of tin are typical examples, there is reason to suppose that *every* hydroxide possesses, in some measure, both acidic and basic character. In the majority of cases this dual role is obscured by the fact that either the basic or the acidic characteristics greatly predominate.

If we can correctly regard silver hydroxide as amphoteric, with the basic character much the more pronounced, we can consider its aqueous solubility in terms of the following two equilibria, whose relative importance will depend on the P_{H} of the solution. In acid or in neutral solutions the reaction represented by



will predominate,³ while in solutions of sufficient alkalinity the solubility will be chiefly in consequence of the equilibrium



To establish the presence of amphoteric properties it becomes necessary to obtain evidence for the existence, in alkaline solutions, of the equilibrium represented by reaction (2). This we have done by measurement of the solubility of silver oxide in pure water and in a wide range of concentrations of sodium hydroxide, potassium hydroxide, barium hydroxide and of alkaline solutions to which various amounts of neutral salts were added.

The Preparation of Reagents

Silver Oxide.—Silver oxide was prepared from 0.05 *N* solutions of silver nitrate and of barium hydroxide⁴ which were dropped simultaneously, from separate reservoirs, into a five-liter reaction vessel containing a liter of conductivity water heated almost to the boiling point. The reagents were dropped at the rate of about 60 drops per minute, care being taken to maintain an equal rate for the two reagents. Except for rubber stoppers, covered with silver foil, which closed the necks of the reaction vessel and of the reagent reservoirs, but were not in direct contact with the solutions, all parts of the preparation system were constructed of Pyrex glass with fused joints. The entire process, including subsequent washings, was carried out in an atmosphere of pure nitrogen. During the reaction period, which extended over about six hours and in which time about 5 g. of silver oxide was produced,⁵ the hot solution in the reaction vessel was stirred with a stream of nitrogen.

(3) We do not mean to imply, however, that the formula for the positive ion containing the dissolved silver is of necessity that written in the equation. For discussion of an anomalous behavior which indicates that it may be necessary to express silver in another form than as Ag^+ , see the discussion contained in a paragraph near the end of this paper.

(4) The preparation of these reagents is described in subsequent paragraphs.

(5) Sufficient for one pair of samples.

After precipitation was completed the silver oxide was transferred, under nitrogen, to a specially designed washing flask (see Fig. 1) of about 500 cc. capacity, where it was given fifteen washings with conductivity water. Usually after about the tenth washing no test for barium was given when a drop of concentrated sulfuric acid was added to 10 cc. of cold wash water. Particular care was exercised during the washing to rid the sample of particles of very fine precipitate, which might show abnormal solubility. To accomplish this the first eight or ten washings were carried out with boiling water in which the precipitate was vigorously shaken and which was then decanted within a few seconds to make sure that the small particles were removed. A sample so prepared would settle out in from three to seven seconds, after vigorous agitation.

Fresh samples of silver oxide were prepared for all solubility determinations in pure water or in dilute alkali. However, in determining solubilities in several of the strong alkali and strong salt solutions, samples which were previously employed in dilute solutions of the same type were carefully rewashed and reemployed.

Alkali.—Baker and Adamson "reagent quality" barium hydroxide was five times recrystallized from conductivity water, in an atmosphere of nitrogen. Potassium and sodium hydroxides were prepared by decomposition of the corresponding amalgams with conductivity water. The amalgams were prepared, out of high grade reagents, by the electrolysis of 50% solutions of alkali, using a platinum anode and a mercury cathode,⁶ and were transferred to the vessel in which they were subsequently decomposed without coming into contact with air. They were rinsed several times with conductivity water before the decompositions were begun.

It was found impracticable to prepare alkaline solutions of higher strength than about 1 *N* by direct decomposition of the amalgams. The more concentrated solutions of alkali were prepared by evaporation of the 1 *N* solutions, in a Pyrex flask, under a pressure of 5–8 cm. of mercury. In order to eliminate the possible influence of silicate contamination which, it was thought, could possibly have occurred during the evaporation process, several strong solutions of potassium hydroxide were prepared by adding to solutions made directly from the "reagent quality" potassium hydroxide sufficient barium hydroxide to precipitate the carbonate. The solubilities obtained with potassium hydroxide prepared in this manner did not differ from those obtained with potassium hydroxide prepared by the evaporation process.

Salts.—Mallinckrodt "reagent quality" silver nitrate and Baker and Adamson "reagent quality" potassium nitrate, potassium sulfate and barium nitrate were employed. Each of these salts was twice recrystallized from conductivity water and was dried in air.

Analytical Reagents.—Standard solutions of nitric and of sulfuric acids were prepared from chlorine-free acids and were stored in glass-stoppered five-pint bottles. Standardizations were made by weight, and were repeated from time to time in the course of the investigations.

Standard solutions of approximately 0.001 *N* potassium iodide were prepared from "reagent quality" material and were standardized against dilute silver nitrate solutions by electrometric titration, under conditions as nearly as possible like those later employed in the solubility determinations. The silver nitrate standards were prepared by controlled dilution of more concentrated solutions which were made up by adding

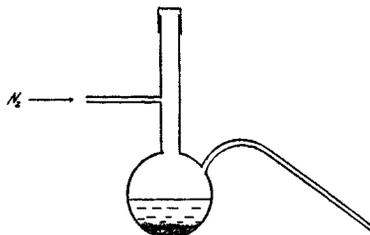


Fig. 1.

(6) Ming Chow, *THIS JOURNAL*, **42**, 488 (1920).

weighed quantities of twice recrystallized and fused silver nitrate to weighed quantities of conductivity water.

Conductivity Water.—Distilled water, previously aerated with carbon dioxide-free air and treated with a few crystals of potassium permanganate to oxidize ammonia, was distilled under a pressure of 5 cm. of mercury in a still of the type described by Bousfield.⁷ The water, so prepared, had a conductivity of from 0.6×10^{-6} mho to 1×10^{-6} mho and was stored in contact with carbon dioxide-free air, in a glass-stoppered green glass bottle. After several weeks of storage the conductivity remained under 2×10^{-6} mho.

The Solubility Apparatus

Solid silver oxide was agitated, in contact with the appropriate solvent, in a shaking device like that described by Randall and Vietti.⁸ All of the manipulations were such as to avoid contact with air and the long necks of the round-bottomed Pyrex flasks (200 cc.) were sealed off with an oxyhydrogen flame. Usually, two samples were brought to equilibrium with each strength of alkali. One flask was placed directly in the shaker in a 25° thermostat and was agitated for from ten to eighteen days, the length of agitation being determined by our experience with the various solvents. The second flask was agitated for four days at about 45° and was then transferred to the 25° thermostat and agitated for another ten to eighteen days. The 25° thermostat maintained a temperature constant to somewhat better than $\pm 0.01^\circ$.⁹ After agitation the flasks were allowed to sediment in a separate 25° ($\pm 0.01^\circ$) thermostat which was free from vibration. From five to seven days were allowed for complete sedimentation.

One of the most important and, at the same time, the most difficult features of the whole research was the filtration process. Best results were finally obtained by siphoning off the clear solution with a carefully regulated nitrogen pressure of from two to three pounds per square inch, which was necessary to force the liquid through the filters at a reasonable rate. With pure alkali in alkalinities below 0.01 *N* and in most alkalinities above 0.4 *N*, a special filter of pure silver was used. This was constructed by reducing in an atmosphere of hydrogen a compressed wad of silver oxide about 5 mm. thick and 15 mm. in diameter and fusing to its edges a cylinder of silver foil. This filter was employed in order to avoid, so far as possible, change of alkalinity at low concentrations of OH⁻ and introduction of silicate at high alkalinities. Filters of unglazed porcelain and of porous Jena glass were used for the intermediate range of alkalinity, since they were somewhat faster. The silver filter was also used with the samples in pure water. Both types of filter were used with the alkaline salt solutions, which ranged in alkalinity from 0.03 to 0.06 *N*. The first several cc. of the solution were always discarded.

A number of the filtered samples were tested, by means of a crude Tyndallometer, for suspended and colloidal matter. Samples which were prepared and filtered in the manner outlined above gave no Tyndall beam and the tests were not continued with later samples. However, an occasional sample did show a solubility which was not in agreement with its mate and which was unreasonably high. In the few instances in which we obtained such obviously erratic values (that ran high by 20% or more) we arbitrarily threw them out as attributable to some lack of care in the filtration.

The Analytical Procedure

A High Precision Potentiometric Method for the Analysis of Traces of Silver.—From 100 to 150 g. of saturated solutions were used for the analysis. The solution was first analyzed for total alkali, by titration with standard acid at a range of concentrations

(7) Bousfield, *J. Chem. Soc.*, **101**, 1452 (1912).

(8) Randall and Vietti, *THIS JOURNAL*, **50**, 1526 (1928).

(9) For description of an efficient but inexpensive device for maintaining good temperature regulation in summer weather, cf. Garrett, *Ind. Eng. Chem.*, **25**, 355 (1933).

suitable for the respective samples, using methyl orange indicator. Corrections were applied for the indicator end-point¹⁰ ($1 \times 10^{-4} N OH^-$) and, where significant, for the acid used in converting AgO^- into Ag^+ . The titrations were made by weight and were corrected to vacuo. The weights employed were standardized by the United States Bureau of Standards.

After the analysis for total alkali the same sample, now barely acid to methyl orange indicator, was employed for the silver analysis. In order to obtain the accuracy desired in the region of lowest solubility, we found it necessary to develop an analytical procedure suitable for the quantitative estimation of traces of silver. We found that potentiometric titration, with a piece of silver foil as an indicator electrode, gave very sharp and reproducible end-points. For the greater portion of the work we used a standard solution of 0.001 *N* potassium iodide for the precipitant.¹¹ The titration was carried out in an ordinary Pyrex beaker. Connection to a calomel half-cell was made by means of a U-tube containing saturated potassium nitrate set in an agar-agar gel. The potassium iodide was added from a 10-cc. microburet with a constricted tip which delivered 50 drops per cc. Reagent was added at exactly three-minute intervals and potentiometer readings were taken just prior to the addition of further reagent. Near the end-point the potassium iodide was added a drop at a time. The titration curves resembled those of the hydrogen electrode in acid-base titration and the end-point was very sharp to a single drop (0.02 cc. of 0.001 *N* potassium iodide). In the range of lowest solubility ($5 \times 10^{-6} N$ silver) about one cubic centimeter was used in titration. Thus the precision was, in the most unfavorable case, about 2%. In the majority of determinations it lay well below 1%.

The reliability of this method of analysis was established by means of an extensive preliminary investigation of a series of "knowns" which were made up to correspond to later samples in so far as added salts were concerned, but to which accurately known dilutions of standard silver nitrate were added. The results were highly satisfactory and gave answers which were correct to within the limits discussed in the previous paragraph. To safeguard against the appearance of unknown factors which might affect the analysis, checks were also run at frequent intervals during the course of the work.

A few practical considerations need to be regarded in the use of this potentiometric method. For example, we found that the presence of bright sunlight changes the point of inflection and makes the titrations entirely untrustworthy, due possibly to a photo-voltaic effect at the electrode.¹² However, by surrounding the beaker with a section cut from a brown glass bottle and covering it with a piece of black paper with holes cut for the buret, stirrer, etc., this source of trouble was easily eliminated. We also found that the sensitivity of the titrations is greatly increased by dipping the silver foil into concentrated nitric acid, but it is necessary, after the cleaning process, to season the electrode by one or two titrations on "known" solutions before it may be put back into use. The end-point e. m. f. is influenced by the presence of salts and by the previous history of the electrode but does not interfere with the reliability of the titrations when the end-

(10) We titrated to the first sharp color change of the indicator and kept a stoppered sample for comparison. In the analysis of samples brought to equilibrium in the absence of alkali (*i. e.*, solubilities in pure water and in neutral salt solutions) the analysis for alkali, in almost every instance, agreed to within one drop with the more sensitive analysis for silver, when the indicator correction was applied.

(11) In the range of higher solubilities we employed 0.005 *N* potassium iodide and, for a portion of the work, used 0.01 *N* potassium bromide. In the latter case we corrected for the solubility of silver bromide, taking account of activity coefficients in the presence of added salts. The correction was small. A similar correction was considered for the solubility of silver iodide but was shown to be negligible.

(12) We expect to study this effect more thoroughly in a later investigation. We are also making a more thorough study of the potentiometric method as a means of measuring traces of halide ions in solution.

point is determined by locating the point at which the maximum deflection is produced per drop of added reagent. The presence of high salt concentrations reduces the sensitivity of the titrations and to this extent limits the precision.

A brief comparative study of the potentiometric method with the nephelometric method, in which we followed the procedure recommended by Lamb, Carleton and Meldrum,¹³ indicated a marked superiority of the potentiometric method for the analysis of silver.

Salt concentrations were not determined by analysis, but were determined from the weights of the respective constituents out of which the solutions were made up.

The Solubility Data

The results obtained are given in the following tables which are, for the most part, self-explanatory. In pure water a total of eleven determinations was made with the silver filter. Several earlier values made with an asbestos filter were discarded although they agree substantially with those made with the more reliable silver filter.

TABLE I

SOLUBILITY (MILLIMOLES OF Ag^+ /1000 G. H_2O) OF Ag_2O IN PURE WATER AT 25°

Undersaturation	Supersaturation	Undersaturation	Supersaturation
0.221	0.218	0.218	0.231
.223	.232	.215	.228
.219	.216	.223	
Av. (U) = .220			Av. (S) = 0.225

Av. 0.222

The average of these eleven determinations (0.222×10^{-3} gram equivalents of silver per 1000 g. of H_2O), we believe to be superior to any of the values which are at present in the literature: 0.216,¹⁴ 0.5¹⁵ (0.216, 0.223, 0.232, 0.295)¹⁶ 0.165.¹⁷

In Tables II to VII, inclusive, the two independent values (one from supersaturation and one from undersaturation) obtained with each pair of samples are shown opposite a common alkalinity. This is an average value of the alkalinity which was actually determined separately for each sample. The effort was made to have the same alkalinity for each member of a pair, by rinsing the moist silver oxide with several portions of the solvent before the flasks were sealed. In some of the earlier work, however, this precaution was neglected so that there really were actual small differences in the alkalinity of the two samples. Where these differences were great enough to affect the solubility beyond the limits of accuracy of the silver determination,¹⁸ the separate solubilities were corrected by the small

(13) Lamb, Carleton and Meldrum, *THIS JOURNAL*, **42**, 251 (1920).

(14) Noyes and Kohr, *Z. physik. Chem.*, **45**, 521 (1903).

(15) Abegg and Cox, *ibid.*, **46**, 1 (1903).

(16) Rebière, *Bull. soc. chim.*, **17**, 309 (1915). The four values are each averages of several determinations with samples of silver oxide prepared in different manners. Apparently no extreme case was taken in any of the preparations. The value of 0.232 was with silver oxide prepared from silver nitrate and barium hydroxide.

(17) Mathur and Dhar, *Z. anorg. allgem. Chem.*, **199**, 389 (1931).

(18) By means of equation 5.

amounts necessary to put them on a common alkalinity basis. The appearance of only one solubility value in a line indicates that either no mate was prepared (at some of the very low alkalinities) or that the mate

TABLE II
SOLUBILITY OF SILVER OXIDE IN AQUEOUS
SODIUM HYDROXIDE

Alkali nor- mality	Silver normality (total) $\times 10^5$		K_c (p_1/p_1^0) $\times 10^8$
	Under- satd.	Super- satd.	
0.0012	...	3.29	..
.0013	2.94
.0023	1.83	...	633
.0101	0.76	...	25.4
.0113	.50	0.58	6.57
.012455	5.86
.0196	.62	.69	4.16
.0223	.67	.67	3.57
.0394	.93	1.01	3.35
.0507	1.01	1.22	2.91
.0566	1.25	1.39	3.57
.0754	1.72	1.80	3.95
.0889	1.83	2.24	4.01
.1174	...	2.62	4.06
.1463	3.44	3.50	4.82
.1807	3.62	...	3.45
.2112	4.01	4.19	3.31
.2726	5.23	...	3.32
.3920	7.38	...	3.29
.3990	7.31	...	3.10
.7485	15.0	14.4	3.65
.7755	14.9	15.7	3.70
1.174	19.3	20.6	2.76
1.276	23.2	21.9	2.98
1.385	24.2	23.1	2.78
1.856	30.7	31.8	2.78
2.330	35.3	38.8	2.42
2.514	34.9	35.0	1.78
2.757	43.6	43.3	2.28
3.219	39.8	41.2	1.44
4.894	47.5	48.3	0.79
6.600	54.0	54.6	.45

TABLE III
SOLUBILITY OF SILVER OXIDE IN AQUEOUS
POTASSIUM HYDROXIDE

Alkali nor- mality	Silver normality (total) $\times 10^5$		K_c (p_1/p_1^0) $\times 10^8$
	U	S	
0.0005	10.3
.0008	...	4.39	..
.0012	...	3.08	..
.0029	1.42	...	163

TABLE III (Concluded)

Alkali nor- mality	Silver normality (total) $\times 10^5$		K_c (p_1/p_1^0) $\times 10^8$
	U	S	
0.0093	0.65	...	17.2
.0095	.63	0.66	17.3
.0098	.53	...	8.16
.0138	.58	.64	6.80
.0205	.60	.67	3.54
.0254	.72	.76	3.72
.0313	.90	.87	4.10
.0457	1.03	1.12	3.26
.0600	1.51	1.40	4.03
.0827	1.76	1.78	3.37
.1225	2.50	2.63	3.56
.1712	3.48	3.62	3.69
.4116	7.96	7.96	3.47
.6708	11.68	12.32	3.03
1.628	25.3	30.0	2.69
2.063	30.8	32.8	2.19
3.006	38.7	...	1.44
3.605	41.3	43.8	1.17
5.007	...	47.0	0.65
5.238	50.9	47.0	.64

TABLE IV
SOLUBILITY OF SILVER OXIDE IN AQUEOUS
BARIUM HYDROXIDE

Alkali nor- mality	Silver normality (total) $\times 10^5$		K_c (p_1/p_1^0) $\times 10^8$
	U	S	
0.0004	17.8
.0007	..	7.37	..
.0016	2.43	3.27	..
.0027	1.28	1.24	200
.0076	0.61	..	22.4
.0153	.65	0.73	8.6
.0178	.69	..	6.1
.0191	.54	.86	5.3
.0208	.69	.69	4.67
.0204	.67	.61	3.65
.0342	.85	.87	3.19
.0413	1.12	1.17	4.74
.0537	1.36	1.32	4.10
.0663	1.52	1.51	3.63
.0939	..	2.04	3.61
.1318	2.81	2.86	3.80
.1630	3.39	3.66	3.98
.2946	5.86	6.01	3.67

was lost in handling or, in a few instances, thrown out for the reason mentioned in a previous paragraph discussing filtration.¹⁹ The last column in each of these tables gives the equilibrium constant, with the activity coefficient ratio neglected, for the supposed reaction (2). In making the calculation the *average* solubility was employed for each pair of samples. This value was also corrected by the constant $2.5 \times 10^{-6} N$ silver which is present in the form of silver hydroxide or some other undissociated form. The basis for this is discussed in a later paragraph. For the vapor pressure of water from potassium hydroxide, from sodium hydroxide, from po-

TABLE V
SOLUBILITY OF SILVER OXIDE IN ALKALINE POTASSIUM NITRATE SOLUTION

Salt normality	Alkaline normality	Silver normality (total) $\times 10^3$		$K_c(p_1/p_1^0) \times 10^3$
		U	S	
0.0120	0.0382	0.98	1.09	4.06
.0302	.0338	.98	0.84	3.82
.0524	.0410	1.22	1.00	4.41
.0690	.0471	1.33	1.47	5.95
.0855	.0413	1.20	1.10	4.75
.104	.0387	1.08	1.15	4.93
.254	.0638	1.64	1.79	5.22
.300	.0358	1.01	0.98	4.14
.415	.0376	0.93	1.06	3.84
.641	.0641	1.55	1.58	4.07
1.02	.0367	1.04	1.03	4.49
1.34	.0648	1.32	1.36	2.73
1.43	.0589	1.58	1.69	4.47
1.85	.0461	1.16	1.06	3.33
2.07	.0644	1.45	1.39	3.14
2.46	.0578	1.72	1.72	6.16
3.01	.0469	1.10	1.14	3.17
3.15	.0567	1.31	1.31	3.22
3.46	.0451	1.16	1.23	4.04
3.71	.0518	1.19	1.22	3.01
3.88	.0521	1.22	1.34	3.42

TABLE VI
SOLUBILITY OF SILVER OXIDE IN ALKALINE POTASSIUM SULFATE SOLUTION

Salt normality	Alkaline normality	Silver normality (total) $\times 10^3$		$K_c(p_1/p_1^0) \times 10^3$
		U	S	
0.0019	0.0492	1.16	1.10	3.20
.0049	.0406	1.05	1.03	3.78
.0090	.0407	1.13	1.23	5.20
.0351	.0434	1.17	1.30	5.08
.0553	.0414	1.05	1.10	3.96
.0795	.0392	1.18	1.04	4.78
.1010	.0554	1.23	1.47	3.91
.1178	.0392	1.07	1.07	4.32

(19) Cf. equation 4.

TABLE VII

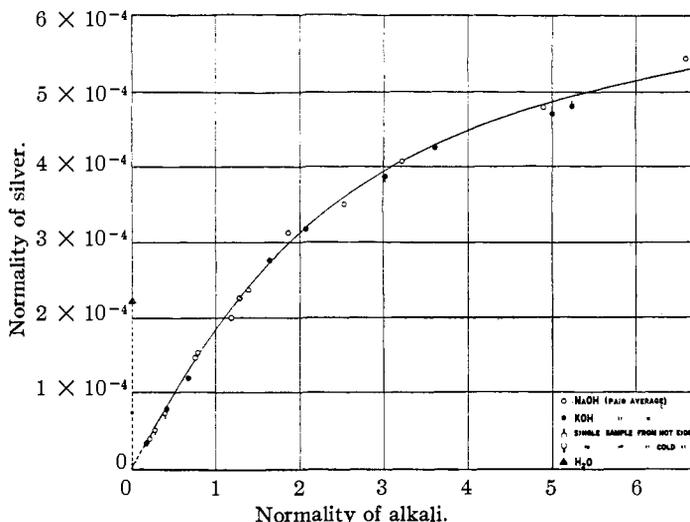
SOLUBILITY OF SILVER OXIDE IN ALKALINE BARIUM NITRATE SOLUTION

Salt normality	Alkaline normality	Silver normality (total) $\times 10^4$		$K_c(p_1/p_1^0) \times 10^4$
		U	S	
0.0011	0.0342	0.85	0.93	3.50
.0016	.0309	.78	.91	3.65
.0033	.0328	.85	1.01	4.29
.0051	.0278	.94	0.91	5.96
.0087	.0354	.98	1.08	4.86
.0254	.0358	1.01	1.03	4.61
.0607	.0325	0.90	0.96	4.36
.0851	.0422	1.07	1.13	4.03
.1749	.0451	1.14	1.19	4.12
.2871	.0440	1.23	1.24	4.88

tassium nitrate, from potassium sulfate and from barium nitrate solutions we employed the values tabulated in the "International Critical Tables."²⁰ For barium hydroxide we assumed Raoult's law, which is sufficiently accurate for our purpose in the range of alkalinity involved.

Discussion and Interpretation of Results

From consideration of the equilibria involved in reactions (1) and (2) it is apparent that if silver hydroxide exhibits amphoteric properties, the solu-

Fig. 2.—Solubility of H₂O in alkali.

bility of silver oxide, as a function of OH⁻ concentration, should (1) fall off rapidly in solutions of low alkalinity, (2) go through a minimum and (3) increase in solutions of higher alkalinity. The data in Tables II, III, and IV, shown graphically in Figs. 2 and 3, show that silver oxide does

(20) "International Critical Tables," Vol. III, p. 373.

exhibit this behavior. From Fig. 3 the position of the minimum can be placed at approximately $0.015 N OH^-$, and at a solubility of about 6×10^{-6} gram equivalent of silver per 1000 grams of water. Within the limits of experimental error no difference was observed in the influences of potassium hydroxide, of sodium hydroxide and of barium hydroxide. In Figs. 2 and 3 *average* solubilities are plotted for each pair of samples except where the tables show only one sample. The latter points are distinguished by vertical (or sloping) lines which indicate whether the equilibrium was established from supersaturation or from undersaturation.

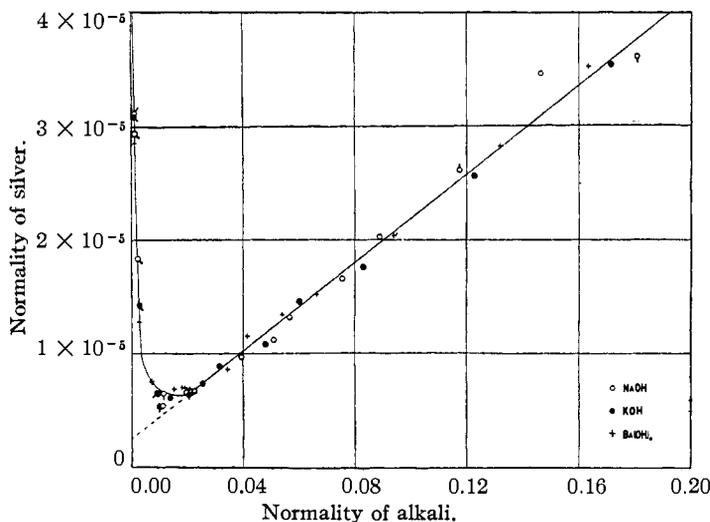


Fig. 3.—Solubility of Ag_2O in alkali.

From the equation for reaction (2) it can be shown that, for the alkaline side of the minimum, the solubility must fit the relationship

$$K_2 = \frac{\gamma_{AgO}^2 m_{AgO}^2 a_{H_2O}}{\gamma_{OH}^2 m_{OH}^2 a_{Ag_2O}} \quad (3)$$

where K_2 is the true equilibrium constant, and is independent of the concentration; γ_{AgO} and γ_{OH} are the activity coefficients of argentate ion and of hydroxyl ion, respectively; m_{AgO} and m_{OH} are the corresponding molalities, expressed as gram ions per 1000 grams of water, and a_{H_2O} and a_{Ag_2O} are the activities of water (from the solution) and of solid silver oxide.²¹ For pressures near atmospheric (at which a_{Ag_2O} becomes unity, by definition) equation (3) may, for convenience, be put in the form

$$K_2 = \left(\frac{\gamma_{MAgO}}{\gamma_{MOH}} \right)^2 \frac{p_1}{p_1^0} K_c \quad (4)$$

(21) The symbols employed in the present paper are consistent with those used by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

where the activity coefficients are now given as "mean activity coefficients" of anion and cation and include the degree of ionization of metallic argentate (MAgO) or of base (MOH); p_1/p_1^0 , which is equal to the activity of water, is the partial pressure of water from the solution divided by the vapor pressure of pure water; and Kc , equal to $(m_{\text{MAgO}}/m_{\text{MOH}})^2$, is the ordinary "Mass Law Constant."

At concentrations of electrolyte not exceeding a few tenths normal, no appreciable error is introduced by putting p_1/p_1^0 equal to one, and at sufficiently low values of the ionic strength the activity coefficient ratio will become unity since the activity coefficient of both argentate and hydroxyl ion will approach the same limiting slope of the Debye-Hückel equation. In this limiting case Kc equals K_2 and equation (4) becomes

$$m_{\text{MAgO}} = \sqrt{K_2} m_{\text{MOH}} \quad (5)$$

We may anticipate that the relationship expressed by equation (5) may hold even at moderate concentrations of alkali since even when γ_{MAgO} and γ_{MOH} depart from the limiting Debye-Hückel slope, we may reasonably expect some resemblance between the activity coefficient curves of two univalent ions of about the same structure, each carrying one atom of oxygen. That equation (5) actually does fit to nearly 1 *N* alkali is shown, in Fig. 2, by the linear dependence of the solubility on OH^- concentration. The curvature which sets in above a normality of 1 indicates that γ_{MAgO} is somewhat larger than γ_{MOH} in high concentrations of alkali.

We have determined K_2 from the square of the slope (*cf.* Equation 5) of the straight line drawn in Fig. 3, which represents that portion of Fig. 2 which is marked by a dotted curve in the neighborhood of the minimum. This yields

$$K_2 = (1.95 \times 10^{-4})^2 = 3.80 \times 10^{-8} \quad (6)$$

We have also calculated the values of $(p_1/p_1^0)Kc$ for the separate pairs of samples. These are recorded with the tabulated data. In making these calculations we have had to take account of the fact that the linear curve of Fig. 3 does not extrapolate to zero solubility for zero normality, but extrapolates, instead, to a silver normality of 2.5×10^{-6} . Equations (4) and (5) apply, of course, only to silver dissolved in the form of argentate ion or its salts. By equation (5) this must go to zero at zero alkalinity. The 2.5×10^{-6} gram equivalent then represents silver dissolved in some other form, present at substantially constant concentration in the alkaline solutions. This is probably undissociated AgOH (or a polymer). At any event the constant 2.5×10^{-6} gram equivalent must be subtracted from the measured solubilities before the latter are employed to calculate $a_{\text{H}_2\text{O}}Kc$ by equation (4). An unweighted average of the twenty-six values in Tables II, III and IV which lie between 0.02 normal alkali and 0.2 normal alkali gives 3.78×10^{-8} for the constant, with extremes of 2.91 and 4.82×10^{-8} . The near constancy which K_2 exhibits at moderate alkalinities indicates the

existence of the equilibrium represented by reaction (2) and establishes the amphoteric character of silver hydroxide.

Taking 3.80×10^{-8} as the most reliable value for K_2 we obtain +10,120 (\approx about 50) calories for the standard free energy change at 298.1°K. in the reaction $\text{Ag}_2\text{O} + 2\text{OH}^- = 2\text{AgO}^- + \text{H}_2\text{O}$.

The interpretation of the data obtained in potassium hydroxide, sodium hydroxide and barium hydroxide solutions is confirmed by the data taken in the presence of salts, although the latter data are somewhat less accurate than those obtained in the absence of salts. (This may have been due in part to non-attainment of equilibrium during the period of agitation for we found it necessary to shake the salts somewhat longer than the pure alkali solutions, but is more probably due to incomplete sedimentation or to poor filtration. We had somewhat more difficulty, in this respect, with salts than with the pure alkali.) Except for those values in Table V which are italicized, the salt data were taken earlier than the majority of our data in pure alkali. The italicized values were taken near the end of our work and are regarded as more reliable than the earlier values. From the nature of the general trend in the salt data we saw little to be gained by repeating the earlier work.

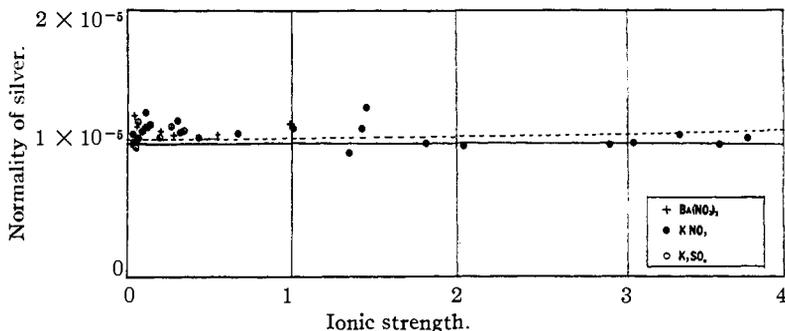


Fig. 4.—Solubility of Ag_2O in 0.04 *N* alkali + salt.

We were a little surprised that the values of $(p_1/p_1^0)Kc$ for the salt solutions did not decrease with increasing ionic strength in the same manner as did the pure alkali values at high concentrations. The fact that the constant is not much affected by even very large increases in the concentration of inert salt indicates that $\gamma_{\text{M}_{\text{Ag}_2\text{O}}}$ is nearly equal to γ_{MOH} even to high ionic strengths in the absence of a large amount of alkali. This is shown more clearly in Fig. 4, where we have plotted the data of Tables V, VI and VII corrected (by means of equation (5)) to a common alkalinity of 0.04 *M*. The dotted line in Fig. 4 is the solubility computed by equation (4) with the ratio set equal to unity. No significance need be attached to the high values at low ionic strength which we think may have been due to the presence of suspended matter. The more reliable data at the opposite

end do indicate, probably correctly, a slight increase in γ_{MAgO} relative to γ_{MOH} .

The reasonably consistent values obtained for $(p_1/p_1^0)Kc$ under a wide variety of conditions rules out, we believe, the contention urged²² in other somewhat similar cases that the increased alkaline solubility may represent colloidal dispersion of the oxide rather than true solution, for it is highly improbable that the extent of colloidal dispersion should correspond quantitatively to the equations which are here fitted under such a variety of conditions.

We also made some solubility measurements in neutral salt solutions. As we would expect from the equilibrium relationship for reaction (1) (where a product and not a ratio of activity coefficients is involved), the solubility of the oxide increases considerably with added salt and this effect is greater for potassium sulfate than for either potassium nitrate or sodium nitrate. However, due probably to the marked influence of the P_{H} value in this region, the data were not very consistent and are not included.

The Dissociation Constant of Argentic Acid.—If we consider the acid dissociation of silver hydroxide by the reaction



we can set up the relationship

$$K_{\text{A}} = a_{\text{H}^+} a_{\text{AgO}^-} / a_{\text{AgOH}} \quad (8)$$

where K_{A} is the dissociation constant of the acid and the other terms are the activities of the respective constituents of the dissociation reaction. Substituting for a_{H^+} its equivalent $\left(\frac{a_{\text{H}_2\text{O}}}{a_{\text{OH}^-}} K_{\text{W}}\right)$, from the dissociation of water and, for a_{AgO^-} its equal, $\sqrt{a_{\text{OH}^-}^2 - a_{\text{Ag}_2\text{O}} K_2 / a_{\text{H}_2\text{O}}}$ from equation (3), we may put equation (8) in the form

$$K_{\text{A}} = \frac{K_{\text{W}} \sqrt{K_2}}{a_{\text{AgOH}}} \sqrt{a_{\text{H}_2\text{O}} a_{\text{Ag}_2\text{O}}} \quad (9)$$

At atmospheric pressure and not too high concentrations of electrolyte this reduces to

$$K_{\text{A}} = K_{\text{W}} \sqrt{K_2} / m_{\text{AgOH}} \quad (10)$$

Taking K_{W} as 1.01×10^{-14} at 25° ,²³ K_2 as 3.80×10^{-8} and m_{AgOH} as 2.5×10^{-6} , we obtain for the dissociation constant of argentic acid at 25° , the value 7.9×10^{-13} , which about corresponds to the third dissociation constant of orthophosphoric acid.

The Anomaly in the Conductivity of Saturated Aqueous Silver Oxide.—From conductivity measurements Böttger²⁴ obtained 1.4×10^{-4} equivalent per 1000 g. of water as the apparent solubility of silver oxide in pure water. This can be brought into line with the more direct solubility determinations

(22) Chatterji and Dhar, *Chem. News*, **121**, 253 (1920).

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

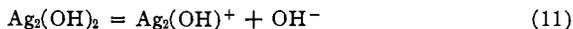
(24) Böttger, *Z. physik. Chem.*, **46**, 521 (1903).

by assuming that 40% of the dissolved oxide remains in the form of undissociated silver hydroxide, which leads to the value 1.96×10^{-8} for the solubility product of silver hydroxide²⁵ at 25°. We have confirmed Böttger's value of the conductivity of the saturated solution by measurements of our own, made with saturated aqueous solutions prepared in identical manner with those which yielded a solubility of 2.22×10^{-4} g. equivalent of silver by our analytical method (*cf.* Table I).

However, our data show that the hypothesis of 60% dissociation of silver hydroxide, in explanation of the conductivity, is not tenable. Thus, if this hypothesis were correct, the addition of alkali (which, except at very high concentration, would be unlikely to affect the saturation value of undissociated silver hydroxide) would repress only the Ag^+ in the saturated solutions and so would lead to a lower solubility limit, at 25°, of about 9×10^{-5} gram equivalent of silver. We actually observed a minimum solubility of about 6×10^{-6} gram equivalent and, by extrapolation of the linear curve in Fig. 3 and by the calculation of the equilibrium constants for reaction (2), we feel confident that we can set about 2.5×10^{-6} gram equivalent of silver as the saturation value of any undissociated form. This value corresponds to 98.9% dissociation in the aqueous solution, which is a more reasonable value to expect for a metallic hydroxide at such low concentration.

The only apparent answer to this dilemma is that, in the saturated aqueous solution of silver oxide and in the saturated solutions in dilute alkali, a considerable amount of the silver must exist in some form other than either Ag^+ or AgOH (AgO^- is also ruled out in dilute alkali and in water, of course). This conclusion is also supported by the calculation of "equilibrium constants" for reaction (1) either on the assumption of complete dissociation into Ag^+ and OH^- or of 60% dissociation of silver hydroxide. Neither solution leads to a satisfactory constant, which indicates that reaction (1) does not represent quite accurately the equilibrium which is present.

We have no experimental evidence of any sort which throws direct light on the nature of this unknown silver carrier. However, it might be worth the suggestion to point out that a rough calculation of an equilibrium constant is not inconsistent with the following hypothetical equilibria



if we make the further assumption that reaction (11) proceeds, in aqueous solution, practically to completion whereas reaction (12) proceeds, except at lower P_{H} , to only a slight extent. Qualitatively, at least, this hypothesis is not inconsistent with the other observations. The hypothesis is also, to some degree, analogous to the known polymerization of mercurous

mercury to form $\text{Hg}_2(\text{OH})_2$, although it is necessary to suppose that the free Ag_2^{++} is not stable, in distinction to the known stability of Hg_2^{++} . We suggest this only as an hypothesis. The suggestion of the equilibria represented by (11) and (12) may prove untenable upon further examination. It does appear definite, however, that some explanation other than either complete dissociation or 60% dissociation of silver hydroxide must be advanced.

The solution of the above dilemma may require a modification of the formulas employed in equations (2), (3), (4) and (5) and may even change numerical values of the constants to conform to the new formulation of the silver carrier, but this will not affect any of the conclusions in the earlier sections of this paper, nor the use of the constants in the calculation of equilibria.

We wish to thank Professor Randall of the University of California for details regarding the construction of the shaking devices of Randall and Vietti and, in particular, Mr. Stanley Abrams, who prepared detailed blue prints of the shakers.

Summary

From the mean of eleven determinations the solubility of silver oxide in pure water is found to be 2.22×10^{-4} gram equivalent per 1000 grams of water at 25° .

The solubility of silver oxide has been measured, at 25° , in solutions of potassium hydroxide, of sodium hydroxide, of barium hydroxide, of alkaline potassium nitrate, of alkaline potassium sulfate and of alkaline barium nitrate. The solubility diminishes rapidly in dilute alkali, reaches a minimum value of about 6×10^{-6} gram equivalent at about 0.015 *N* alkali, increases in a linear fashion up to about 1.0 *N* alkali and increases more slowly above that value. Within the limits of experimental error the solubilities are the same in potassium hydroxide, in sodium hydroxide and in barium hydroxide of equal normalities. In alkaline solutions the addition of inert salts does not appreciably influence the solubility.

The data indicate clearly that silver hydroxide possesses weak acid properties. The equilibrium constant for the reaction $\text{Ag}_2\text{O} + 2\text{OH}^- = 2\text{AgO}^- + \text{H}_2\text{O}$ has been found to be 3.80×10^{-8} . The standard free energy change for the same reaction is +10,120 (≈ 50) calories. The dissociation constant for argentic acid is 7.9×10^{-13} .

A potentiometric method suitable for determining traces of silver (or of halides) has been described.

From the anomalous conductivity of saturated aqueous silver oxide it is pointed out that silver must be present in that solution in the form of some ion, or molecule, as yet unidentified.