D_6^4–P$6_2$22 and D_6^5–P$6_4$22. Of these space groups the first two and the latter two result in enantiomorphic pairs of identical structures. Enantiomorphic structures are indistinguishable by the powder methods used. Choosing a space group with the higher symmetry, all calculations were performed on D_6^4–P$6_2$22. Satisfactory agreement with experiment was obtained.

Relative intensities were calculated from the relation

$$I_o = \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}\, p\, |F_{\mathrm{hkl}}|^2 K$$

where θ is the Bragg angle, p is the multiplicity, F_{hkl} is the structure factor and K is a proportionality constant.

Crystallographic data for $NbGe_2$ are shown in Table II. Atoms are in the following positions, 3 Nb in (d): $^1/_2, 0, ^1/_2;\ 0, ^1/_2, ^1/_6;\ ^1/_2, ^1/_2, ^5/_6$ and 6 Ge in (j): $x, 2x, ^1/_2;\ 2\bar{x}, \bar{x}, ^1/_2;\ x, \bar{x}, ^5/_6;\ \bar{x}, 2\bar{x}, ^1/_2;\ 2x, x, ^1/_6;\ \bar{x}, x, ^5/_6$. The value $^1/_6$ was chosen for x. No attempt was made to refine the parameter.

Each niobium atom in $NbGe_2$ has four germanium atoms at 2.68 Å., six germanium atoms at 2.87 Å. and four niobium atoms at 3.36 Å. Each germanium atom is surrounded by two germanium and two niobium atoms at 2.68 Å., three germanium and three niobium atoms at 2.87 Å. and four germanium atoms at 3.36 Å.

A diffraction pattern of Nb_3Ge corresponds very closely in both spacings and intensities to the patterns of Mo_3Ge[9] and Mo_3Si[10] which have the cubic "β-tungsten" structure. For Nb_3Ge the lattice constant is a = 5.168 ± 0.002 Å. Water displacement yielded a density of 8.17 g./ml. The theoretical density is 8.47 g./ml. assuming two molecules of Nb_3Ge per unit cell.

Calculated intensities agree well with the observed intensities and consequently fix the space group for Nb_3Ge as O_h^3–Pm3n with atoms in the positions 2 Ge in (a): $0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2$ and 6 Nb in (c): $^1/_4, 0, ^1/_2;\ ^1/_2, ^1/_4, 0;\ ^3/_4, 0, ^1/_2;\ 0, ^1/_2, ^1/_4;\ ^1/_2, ^3/_4, 0;\ 0, ^1/_2, ^3/_4$. Each germanium atom in Nb_3Ge is surrounded by 12 niobium atoms at a distance of 2.89 Å. Each niobium atom has two niobium atoms at 2.58 Å., four germanium atoms at 2.89 Å. and eight niobium atoms at 3.17 Å.

Chemical Properties

The niobium germanides were tested for reactivity with a variety of common chemicals. Solutions were placed in contact with the germanides overnight and then were heated. All the compounds reacted readily with fused sodium carbonate and fused sodium hydroxide. All reacted with hydrofluoric acid (48%), hydrogen peroxide solution (30%) and sodium hydroxide solutions in the cold. Only $NbGe_{0.64}$ failed to react with concentrated hydrochloric acid. Concentrated sulfuric acid reacted with $NbGe_2$ and Nb_3Ge when hot after failing to react cold. All the niobium germanides were unreactive toward concentrated hydriodic acid, nitric acid (concentrated or dilute), 6 N sulfuric acid, dilute hydrochloric acid and aqua regia. The niobium germanides react with more of these reagents than do molybdenum germanides[5] and tantalum germanides,[11] although the niobium germanides are thermodynamically more stable.[7]

Acknowledgment.—We are greatly indebted to Professor Hans Nowotny for discussions of the phase composition data.

BERKELEY, CALIFORNIA

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[9] A. W. Searcy, R. J. Peavler and H. J. Yearian, THIS JOURNAL, **74**, 566 (1952).

[10] D. H. Templeton and C. H. Dauben, *Acta Cryst.*, **3**, 261 (1950).

[11] J. M. Criscione, Ph.D. Thesis, Purdue University.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Equilibria in Alkaline Argentocyanide Solutions

BY I. M. KOLTHOFF AND J. T. STOCK

RECEIVED DECEMBER 5, 1955

In the presence of strong alkali, silver and argentocyanide ions react according to $Ag^+ + 2OH^- + Ag(CN)_2^- \rightleftarrows 2Ag\substack{(OH)\\(CN)}^-$. At 25° the formation constant $K_A = \left[Ag\substack{(OH)\\(CN)}^-\right]^2/[Ag^+][OH^-]^2[Ag(CN)_2^-] = 3.4 \pm 0.8 \times 10^6$. The instability constant of the hydroxyargentocyanide ion $K_{Hy} = [Ag^+][OH^-][CN^-]/\left[Ag\substack{(OH)\\(CN)}^-\right] = 6 \times 10^{-14}$. The solubility product of silver cyanide is calculated as $2.3 \pm 1 \times 10^{-16}$.

In an examination of the mechanism of the amperometric argentometric titration of cyanide in sodium hydroxide medium,[1] we observed that argentocyanide greatly increases the solubility of silver hydroxide and of silver cyanide. In the present paper it is shown that this effect is due to the reaction

$$Ag^+ + 2OH^- + Ag(CN)_2^- \rightleftarrows 2Ag\substack{(OH)\\(CN)}^- \quad (A)$$

We have determined the equilibrium constant K_A of this reaction and have also obtained a value for the solubility product of silver cyanide.

Experimental

C.P. reagents and conductivity water were used in the preparation of all solutions. Apart from the data shown in Table IV and in Figs. 2 and 3, which were obtained with air-containing solutions at room temperature (approximate range 22 to 25°), all observations refer to solutions at 25.0 ± 0.1° which were deoxygenated by means of a stream of nitrogen.

The approximately 0.2 M potassium cyanide stock solution was standardized daily.[2] Portions of the stock solution were diluted as required with sodium hydroxide solution. Potassium argentocyanide solutions were prepared as needed by mixing the calculated volumes of potassium

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[1] H. A. Laitinen, W. P. Jennings and T. D. Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 574 (1946).

[2] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 574.

cyanide and silver nitrate solutions. The apparatus for the measurement of current–voltage (c.v.) curves was the same as in previous work.[3] All potentials were measured with reference to the saturated calomel electrode (S.C.E.). The sensitivity of the platinum wire micro-electrode, which was rotated at 600 r.p.m., was 136 μa. per millimole of silver per liter in 0.01 *M* potassium nitrate at 25.0°. The electrode was stored in 10 *M* nitric acid and, before use, was short-circuited in 0.1 *M* perchloric acid against the S.C.E. until the current became very small,[4] rinsed and heavily silver-plated.[5]

The manual voltammetric apparatus was similar to that of Kolthoff and Lingane,[6] except that a microammeter (30 μa. range; Weston Electrical Corp.), read with an accuracy of 0.05 μa., was used when the maximum current exceeded about 5 μa.

Results and Discussion

Argentometric Titration of Alkaline Argentocyanide Solutions to Turbidity Point.—On adding silver nitrate to sodium hydroxide solution containing argentocyanide, the cathodic current at a silver-plated rotating micro-electrode maintained at a suitable potential (−0.15 volt *vs.* S.C.E. was used throughout the present work) at first increases linearly with the concentration of added silver. Continued addition of silver causes a reduction in the slope of the reagent line, as shown in Fig. 1, and the appearance of a turbidity. The concentration of added silver (hereinafter referred to as the "turbidity concentration") at the point of intersection of the two portions of the amperometric titration line corresponds quite closely with and is a little smaller than the concentration required to produce the first perceptible permanent turbidity (see arrows in Fig. 1). The reproducibility of the amperometric end-point is about ± 1 × 10^{-5} *M*.

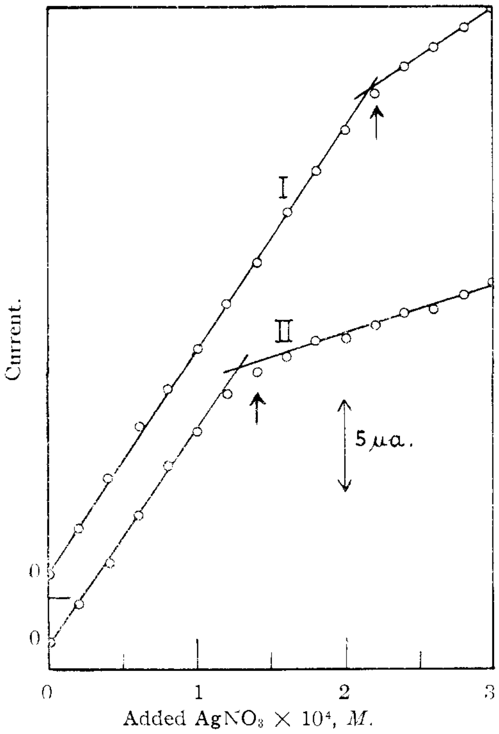

Fig. 1.—Amperometric turbidity titration of alkaline argentocyanide solutions: I, 2 × 10^{-3} *M* argentocyanide in 0.1 *M* sodium hydroxide. First permanent turbidity at arrow; II, as I, but in 0.05 *M* sodium hydroxide.

The "turbidity concentration" increases with increasing sodium hydroxide concentration (see Fig. 1). In a 0.004 *M* argentocyanide solution between the approximate limits 0.1 and 0.5 *M* of sodium hydroxide, the relationship was found to be linear. Johnston, Cuta and Garrett[7] found that over a somewhat wider range of alkali concentrations the solubility of silver oxide in sodium hydroxide solution likewise follows a linear relationship, the dissolved silver existing mainly in the form of the argentate ion, AgO^-. We have determined the "turbidity concentration" in argentocyanide-free sodium hydroxide solutions and our results agree closely with the solubility data of Johnston, *et al.* Evidently argentocyanide greatly increases the solubility of silver in the presence of strong alkali. Further, whereas the turbid argentocyanide-free solutions gave black deposits on standing in the dark, most of the deposits from argentocyanide-containing solutions were white in color.

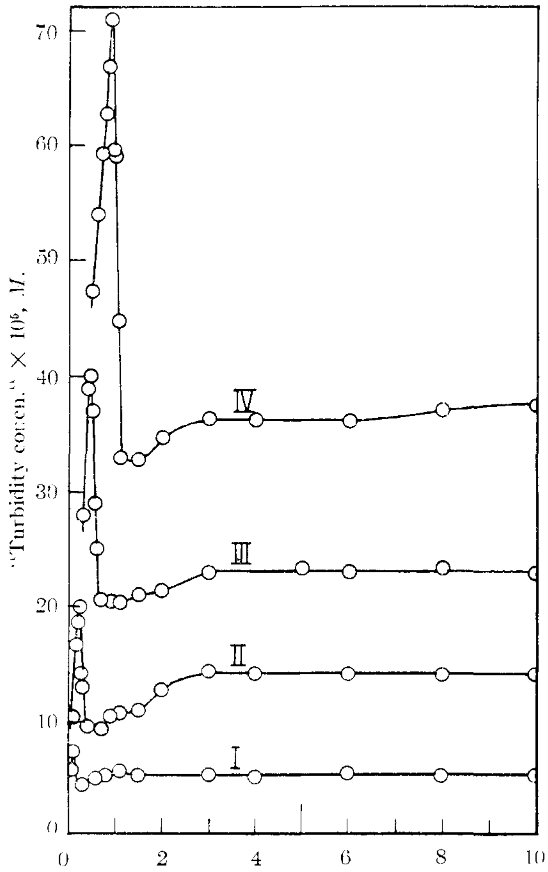

Fig. 2—Effect of argentocyanide concentration on "turbidity concentration": I, in 0.02 *M* sodium hydroxide; II, 0.05 *M*; III, 0.10 *M*; IV, 0.2 *M*.

At a given sodium hydroxide concentration the "turbidity concentration" first increases markedly

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[3] I. M. Kolthoff and J. T. Stock, *The Analyst*, in print.

[4] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, **26**, 632 (1954).

[5] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **53**, 1524 (1936).

[6] I. M. Kolthoff and J. J. Lingane, *ibid.*, **61**, 825 (1939).

[7] H. L. Johnston, F. Cuta and A. B. Garrett, *ibid.*, **55**, 2311 (1933).

with increasing argentocyanide concentration, passing through a sharp peak, the height and position of which depend on the concentration of sodium hydroxide. The steep initial portions of the curves shown in Fig. 2 are not linear; the slopes diminish with increasing argentocyanide concentration. With further increase of argentocyanide concentration the turbidity concentration drops markedly and soon attains a constant value which increases linearly with sodium hydroxide concentration.

A probable explanation of these results is that, in alkaline solution, argentocyanide is partially and reversibly converted into hydroxyargentocyanide

$$\mathrm{Ag(CN)_2^-} + \mathrm{OH^-} \rightleftharpoons \mathrm{Ag}^{(\mathrm{OH})^-}_{(\mathrm{CN})} + \mathrm{CN^-} \qquad \text{(B)}$$

Cyanide thereby released is available for sequestering added silver

$$\mathrm{Ag^+} + \mathrm{OH^-} + \mathrm{CN^-} \rightleftharpoons \mathrm{Ag}^{(\mathrm{OH})^-}_{(\mathrm{CN})} \qquad \text{(C)}$$

The over-all reaction for the take-up of added silver ions is thus (A).

The expression for the equilibrium constant of reaction (A), *viz.*

$$\frac{\left[\mathrm{Ag}^{(\mathrm{OH})^-}_{(\mathrm{CN})}\right]^2}{[\mathrm{Ag^+}][\mathrm{OH^-}]^2[\mathrm{Ag(CN)_2^-}]} = K_\mathrm{A} \qquad (1)$$

is simplified when silver cyanide (AgCN) is precipitating. At the turbidity point $[\mathrm{Ag^+}]\,[\mathrm{CN^-}] = S_{\mathrm{AgCN}}$, the solubility product of silver cyanide. Equation 1 then becomes

$$\frac{K_{\mathrm{In}}x^2}{S^2_{\mathrm{AgCN}}[\mathrm{OH^-}]^2} = K_\mathrm{A} \qquad (2)$$

where $x = \left[\mathrm{Ag}^{(\mathrm{OH})^-}_{(\mathrm{CN})}\right]$ and K_{In} the instability constant of the argentocyanide ion, *viz.*, $[\mathrm{Ag^+}][\mathrm{CN^-}]^2/[\mathrm{Ag(CN)_2^-}]$. The "turbidity concentration" should thus be proportional to the hydroxyl ion concentration (assumed to be equal to the concentration of sodium hydroxide), as was found. This conclusion is not altered if the precipitating solid is regarded as silver argentocyanide, $\mathrm{Ag[Ag(CN)_2]}$. In the calculation of K_A activity coefficients have not been introduced since both the numerator and denominator in equations 2 and 3 contain the square of the activity coefficient of a univalent ion. The reported values of K_A therefore correspond to an ionic strength of zero.

Unlike the stronger solutions, very dilute argentocyanide solutions (in which the "turbidity concentration" increases rapidly with increasing argentocyanide concentration) give a *black* deposit on standing. This suggests that, in such cases, silver (hydr)oxide is the separating solid. Under these conditions equation 1 becomes

$$\frac{x^2}{S_{\mathrm{AgOH}}[\mathrm{OH^-}][\mathrm{Ag(CN)_2^-}]} = K_\mathrm{A} \qquad (3)$$

where S_{AgOH} is the solubility product of silver hydroxide. According to equation 3 the "turbidity concentration" should increase with an increase in concentration of either hydroxyl or of argentocyanide; that this occurs is shown by the curves in Fig. 2.

Systems Containing Bromide.—Further information was obtained by repeating the experiments in the presence of a known concentration of potassium bromide. Under our conditions silver bromide separates at the turbidity point and the reproducibility of the amperometric end-point improved to about $\pm 5 \times 10^{-6}$ *M*. Instead of equation 1 we write

$$\frac{x^2[\mathrm{Br^-}]}{S_{\mathrm{AgBr}}[\mathrm{OH^-}]^2[\mathrm{Ag(CN)_2^-}]} = K_\mathrm{A} \qquad (4)$$

where S_{AgBr} is the solubility product of silver bromide. When silver bromide separates at the turbidity point the "turbidity concentration" should vary with the square roots of the concentrations of bromide and argentocyanide and with the first power of the concentration of hydroxyl. These relationships were found to hold.

Since well-established data for S_{AgBr} are available, we have used equation 4 for the evaluation of K_A. In all the experiments the value of x is equal to twice the turbidity concentration t (see equation 1) minus a correction c for the formation of argentate: $x = 2t - c$. For alkaline solutions saturated at 25° with silver oxide the data of Johnston, *et al.*, give as the concentration c of dissolved silver

$$c = 1.95 \times 10^{-4}\,[\mathrm{OH^-}] + 2.5 \times 10^{-6} \qquad (5)$$

the numerical term being attributed to dissolved but undissociated silver hydroxide. When the solubility of silver (hydr)oxide is not exceeded, c will be smaller than in equation 5 and is given by the expression

$$c = 1.95 \times 10^{4}\,\frac{[\mathrm{Ag^+}][\mathrm{OH^-}]^2}{S_{\mathrm{AgOH}}} + y \qquad (6)$$

where y is a quantity less than 2.5×10^{-6}. When the turbidity is due to the separation of silver bromide, equation 6 becomes

$$c = 1.95 \times 10^{-4}\,\frac{S_{\mathrm{AgBr}}[\mathrm{OH^-}]^2}{S_{\mathrm{AgOH}}[\mathrm{Br^-}]} + y \qquad (7)$$

In solutions containing bromide, the highest sodium hydroxide concentration employed was 0.3 *M*, the smallest bromide concentration being 0.001 *M*. Introducing these figures into equation 7 and taking S_{AgBr}[8] $= 5.0 \times 10^{-13}$ and $S_{\mathrm{AgOH}} = 1.5 \times 10^{-8}$ (present work), the *maximum* argentate correction is seen to be about 5×10^{-7} *M;* at this low concentration of argentate, y is negligible.

It is easily seen from equation 1 that at the turbidity point

$$[\mathrm{Ag(CN)_2^-}] = [\mathrm{Ag(CN)_2^-}]_{\mathrm{init}} - {}^1\!/_2 x \qquad (8)$$

where $[\mathrm{Ag(CN)^-}]_{\mathrm{init}}$ is the initial argentocyanide concentration corrected for the slight dilution effect.

Three sets of titrations with formation of silver bromide at the turbidity point were performed, the initial concentrations of argentocyanide, bromide and hydroxide in turn being made the variable to be studied. The results are summarized in Tables I, II and III. The over-all average value of the equilibrium constant K_A of reaction (A) at 25° is found to be $3.4 + 0.8 \times 10^6$.

The equilibrium constant, K_B, of reaction (B), *viz.*, $\left[\mathrm{Ag}^{(\mathrm{OH})^-}_{(\mathrm{CN})}\right][\mathrm{CN^-}]/[\mathrm{Ag(CN)_2^-}][\mathrm{OH^-}]$ is given by

$$K_\mathrm{B} = K_\mathrm{A}^{1/2}K_{\mathrm{In}}^{1/2} \qquad (9)$$

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[8] B. B. Owen and S. R. Brinkley, THIS JOURNAL, **60**, 2233 (1938).

Taking $K_{In} = 1.4 \times 10^{-20}$, the value calculated by Ricci,[9] K_B is thus 2×10^{-7}. Similarly the instability constant, K_{Hy}, of the hydroxyargentocyanide ion, *viz.*, $[Ag^+][OH^-][CN]/\left[Ag\begin{matrix}(OH)^-\\(CN)\end{matrix}\right]$, is given by

$$K_{Hy} = K_{In}^{1/2}/K_A^{1/2} \qquad (10)$$

and has the value 6×10^{-14}.

Calculation of the Solubility Product of Silver Cyanide.—Insertion of the experimental value of K_A into equation 2 permits a calculation of the solubility product of silver cyanide. This is of interest, since the value of this solubility product is uncertain.[9] In the experiments with bromide-free 0.004 M argentocyanide in sodium hydroxide solutions of varying concentration, the maximum argentate correction, calculated analogously to that for bromide-containing systems, was about 2×10^{-6} M. The average value of S_{AgCN} in Table IV is calculated to be $2.3 \pm 1 \times 10^{-16}$ at 22 to 24°. This value compares reasonably with the value 1.2×10^{-16}, calculated by Ricci[9] from selected data in the literature.

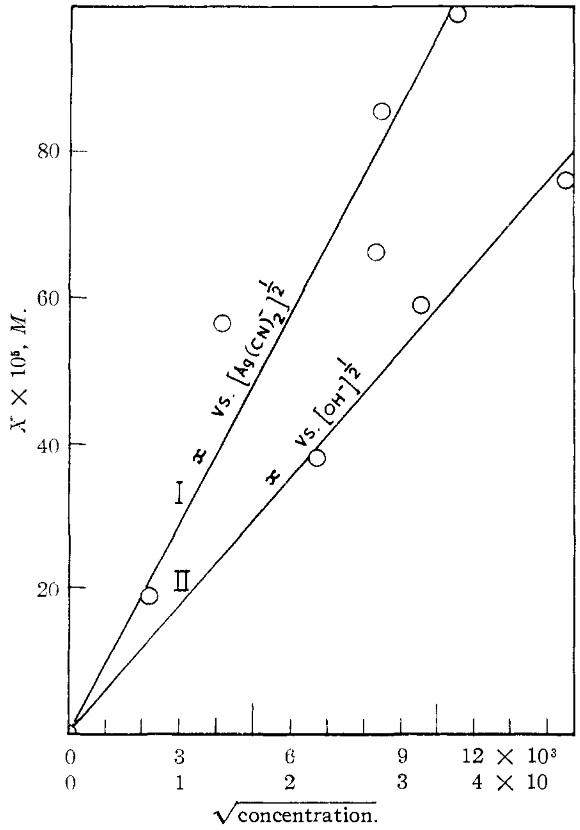

Fig. 3.—"Turbidity concentration" relationships in systems of low argentocyanide concentration: I (upper concentration scale), argentocyanide in 0.2 M sodium hydroxide; II (lower scale); $[Ag(CN^-)_2] = 6 \times 10^{-5}$ M at turbidity point at varying [NaOH].

TABLE I

VARIATION OF HYDROXYARGENTOCYANIDE CONCENTRATION (x) WITH ARGENTOCYANIDE CONCENTRATION

0.001 M bromide in 0.1 M sodium hydroxide

$[Ag(CN)_2^-] \times 10^3$, M Initial	Final	$x \times 10^5$, M	$K_A \times 10^{-6}$
0.3	0.26	7	3.9
0.6	0.55	10	3.9
0.8	0.74	12	3.8
1.0	0.93	14	4.0
1.4	1.32	15	3.6
2.0	1.91	17	3.1
2.6	2.50	19	3.0
3.0	2.89	22	3.2
3.5	3.39	23	3.1
4.0	3.87	26	3.4
5.0	4.85	30	3.8
6.5	6.33	34	3.7
10.0	9.77	45	4.1
		Av.	3.6×10^6

TABLE II

VARIATION OF HYDROXYARGENTOCYANIDE CONCENTRATION (x) WITH BROMIDE CONCENTRATION

0.002 M argentocyanide in 0.1 M sodium hydroxide

$[Br^-] \times 10^3$, M	$[Ag(CN)_2^-] \times 10^3$, M	$x \times 10^5$, M	$K_A \times 10^{-6}$
1.0	1.91	18	3.3
1.5	1.93	14	3.1
2.0	1.94	12	2.8
3.0	1.96	9	2.3
4.0	1.96	7	2.1
5.0	1.97	7	2.3
6.0	1.97	7	2.6
7.0	1.97	6	2.2
8.0	1.97	5	2.2
8.5	1.98	5	1.9
10.0	1.98	5	2.1
		Av.	2.5×10^6

TABLE III

VARIATION OF HYDROXYARGENTOCYANIDE CONCENTRATION (x) WITH HYDROXIDE CONCENTRATION

0.002 M bromide and 0.004 M argentocyanide

$[OH^-]$, M	$[Ag(CN)_2^-] \times 10^3$	$x \times 10^5$, M	$K_A \times 10^{-6}$
0.06	3.93	13	4.8
.08	3.92	17	4.5
.10	3.89	22	4.9
.12	3.88	24	4.2
.14	3.87	27	3.8
.16	3.84	32	4.0
.18	3.83	35	3.9
.21	3.80	40	3.8
.25	3.78	45	3.4
.30	3.74	52	3.2
.50	3.59	81	3.0
		Av.	4.0×10^6

By application of equation 3 to the limited data obtained in solutions of very low argentocyanide concentration, the solubility product of silver hydroxide may be calculated. At the turbidity point, these solutions are saturated with silver hydroxide, so that the argentate correction c, given directly by equation 5, is definitely significant. However, since the concentration of hydroxyargentocyanide at the turbidity point may be as much as eight times the concentration of argentocyanide, the value of the

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[9] J. E. Ricci, *J. Phys. Colloid Chem.*, **51**, 1375 (1947).

TABLE IV

VARIATION OF HYDROXYARGENTOCYANIDE CONCENTRATION (x) WITH HYDROXIDE CONCENTRATION

Initial argentocyanide concentration, 0.004 M, bromide absent.

[NaOH], M	$x \times 10^6$, M	$S_{AgCN} \times 10^{16}$
0.1	23	3.0
.15	30	2.6
.2	36	2.3
.3	51	2.2
.4	67	2.1
.5	81	2.1
.6	108	2.3
.7	118	2.1
.8	145	2.3
.9	167	2.4
	Av.	2.3×10^{-16}

latter is known with considerably less accuracy than in the experiments in Tables I, II and III. Nevertheless, with less than 0.001 M of initial argentocyanide in 0.2 M sodium hydroxide, a plot of x against the square root of the argentocyanide concentration (at turbidity point) gives points which lie about the straight line shown as curve I in Fig. 3. Used in conjunction with equation 3, the slope of this line yields $1.4 \pm 1 \times 10^{-8}$ as the value of S_{AgOH}. Experiments in more dilute sodium hydroxide solution were used to obtain x at an argentocyanide concentration at turbidity point of 6×10^{-5} M. A plot of x against the square root of the sodium hydroxide concentration likewise appears to be linear, as shown by curve II, Fig. 3. The values of S_{AgOH} calculated from the slope of this curve is $1.6 \pm 1 \times 10^{-8}$. These values, obtained at 22 to 25°, are approximate only. They are of the same order as the generally-accepted value, *viz.*, 2×10^{-8} and therefore could provide additional quantitative support for the scheme of reaction.

In a future paper we intend to discuss the significance of the present results in an interpretation of the argentometric amperometric titration of cyanide.

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rotated Dropping Mercury Electrode as a New Electrode in Polarography

BY W. STRICKS AND I. M. KOLTHOFF

RECEIVED DECEMBER 5, 1955

The design, operation and characterisitics of a rotated dropping mercury electrode are described. The characteristics of current–voltage curves obtained at the new electrode differ from those observed at the conventional dropping mercury electrode. The effects of surface active substances, ionic strength and other factors on the limiting current are described and compared with those observed at the conventional dropping electrode. In a given supporting electrolyte limiting currents of various metal ions in the absence of surface active substances are proportional to the square root of their diffusion coefficients. The change of the limiting current with applied voltage is quite different from that observed at the conventional electrode. This is attributed to stirring effects. In the presence of suitable capillary active substances (gelatin), the c.v. curve has an appearance similar to that at the conventional dropping electrode. The limiting current of metal ions is proportional to concentration in the range 5×10^{-6} to 8×10^{-4} M. The half-wave potentials of metal ions both in the presence and absence of gelatin are independent of the concentration and slightly more negative than those observed at the conventional electrode. The analysis of the thallium wave is the same at the rotated as at the conventional electrode. The high sensitivity and the simple operation make the new electrode extremely useful for the analysis of electroactive substances at very low concentrations. For analytical purposes it is recommended to suppress stirring by addition of a suitable surface active substance. Even though the limiting current in the presence of such a substance is only about one half of that found in its absence, the new electrode is under these conditions of the order of ten times more sensitive than the conventional electrode.

Introduction

We developed a rotated dropping mercury electrode in which the mercury is dislodged in an upward direction into the solution from the tip of a rotated U-tube, the droptime being controlled by the dimensions of the electrode and by the speed of rotation. The new electrode which is denoted as R.D.M.E. combines the advantages of the conventional dropping mercury electrode D.M.E. with those of the rotated platinum electrode. The hydrogen overvoltage and precision of the new electrode are the same as those of the D.M.E., but the sensitivity of the R.D.M.E. can be made at least 10 times greater than that of the D.M.E. This increased sensitivity makes the R.D.M.E. more suitable for trace analysis. Electroactive species in solutions as dilute as 5×10^{-6} M can be detected and determined. In amperometric titrations it can be used at dilutions of the same order of magnitude as the rotated platinum electrode. The construction and manipulations of the new electrode are simple and it can therefore be used for routine work. In contrast to the conventional electrode the R.D.M.E. can be used without any modification for the analysis of systems with flowing liquids. For theoretical studies of electrode reactions the R.D.M.E. should be equally useful as the D.M.E. Moreover, the former provides valuable information on streaming effects at the interface mercury–solution and adsorption and desorption of capillary active substances.

The characteristics of the new electrode differ in many respects from those of the D.M.E. Thus the shape of the current–voltage curves is greatly affected by the concentration of supporting electrolyte and by the presence of capillary active substances. At low ionic strength and in the absence of surface active substances the limiting currents of