of molecular weight for the acids considered, it would be expected on the basis of Hildebrand's equation that the "B"'s would be in the order of the molecular weights. This is in accordance with experimental finding, shown graphically in Fig. 4.

Summary

A method of extrapolating ionization constants determined by the conductance method has been suggested. The method consists of plotting the logarithm of the ionization constant, which includes the ion activity coefficient calculated by the Debye–Hückel limiting law, against the concentration of undissociated electrolyte. The validity of the method is based mainly on empirical evidence which indicates the linearity of such a plot up to high concentrations in the case of the organic acids considered.

The thermodynamic ionization constants of cyanoacetic, formic, and butyric acids in aqueous solution at 25° have been measured by the conductance method and found to be

Cyanoacetic acid	3.360×10^{-3}
Formic acid	1.825×10^{-4}
Butyric acid	1.518×10^{-5}

RECEIVED FEBRUARY 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, AND THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Polarographic Study of the Reduction of Chromate Ion at the Dropping Mercury Electrode

BY JAMES J. LINGANE AND I. M. KOLTHOFF

The purpose of this study was to investigate the reduction of chromate ions at the dropping mercury electrode by means of the polarographic technique.[1] The only previous study of the reduction of chromate at the dropping electrode is found in a recent paper of Thanheiser and Willems,[2] which appeared after the present investigation was begun. These authors studied the reduction of chromate only in sodium hydroxide medium, with particular reference to the polarographic determination of chromium in steel. We have investigated the reduction of chromate in unbuffered solutions and in the presence of buffers, as well as in strongly alkaline medium, and have discovered several new and interesting phenomena.

Experimental

The current–voltage curves (polarograms) were obtained and photographically recorded by means of a standard Heyrovsky polarograph.[1] Most of the polarograms were obtained by using an external saturated calomel electrode as anode, rather than the customary stationary pool of mercury on the bottom of the cell, in order to minimize contact of the chromate solutions with mercury. The H-cell and dropping electrode arrangement described by Lingane and Laitinen[3] was used. The cell was kept in a water thermostat at 25 ± 0.1°, and air was displaced from the solutions with nitrogen. Reagent grade chemicals and conductivity water were used in preparing all solutions.

In most of the experiments the pressure on the dropping mercury, hereinafter designated by h, was maintained at 72.0 ± 0.2 cm. of mercury. The amount of mercury flowing from the dropping electrode per sec. under a pressure of 72 cm. designated by m, was determined by the method already described.[1,4] Two different capillaries were used, for which the values of m were, respectively, 1.54 and 1.58 mg. sec.$^{-1}$ at $h = 72$ cm.

The drop time, in dilute potassium chloride solution with the dropping electrode disconnected from the polarizing e. m. f., was 4.2 ± 0.1 sec. The drop time occasionally became erratic, especially in neutral or slightly acid chromate solutions. This probably was caused by the wetting of the interior of the capillary by the chromate solution when the mercury thread retracts momentarily into the lumen after each mercury drop falls. This erratic behavior was eliminated by dipping the tip of the capillary into concentrated nitric acid, and then washing with water, while the mercury was issuing from the tip. The erratic dropping also could be eliminated by simply polarizing the dropping electrode cathodically for a few seconds at a potential of about -1.5 v.

The current-recording galvanometer of the polarograph was calibrated carefully by the method already described.[4]

Reduction of Chromate in Alkaline Medium.— In unbuffered solutions of potassium chromate, with potassium chloride as the supporting electrolyte, the c. v. curve of chromate consists of several waves as shown by curve 1 in Fig. 1.

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[1] For a review of the polarographic method, see I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1–94 (1939).

[2] G. Thanheiser and J. Willems, *Mitt. Kaiser Wilhelm Inst. Eisenforsch. (Düsseldorf)*, **21**, 65 (1939).

[3] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal., Ed.*, **11**, 504 (1939).

[4] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

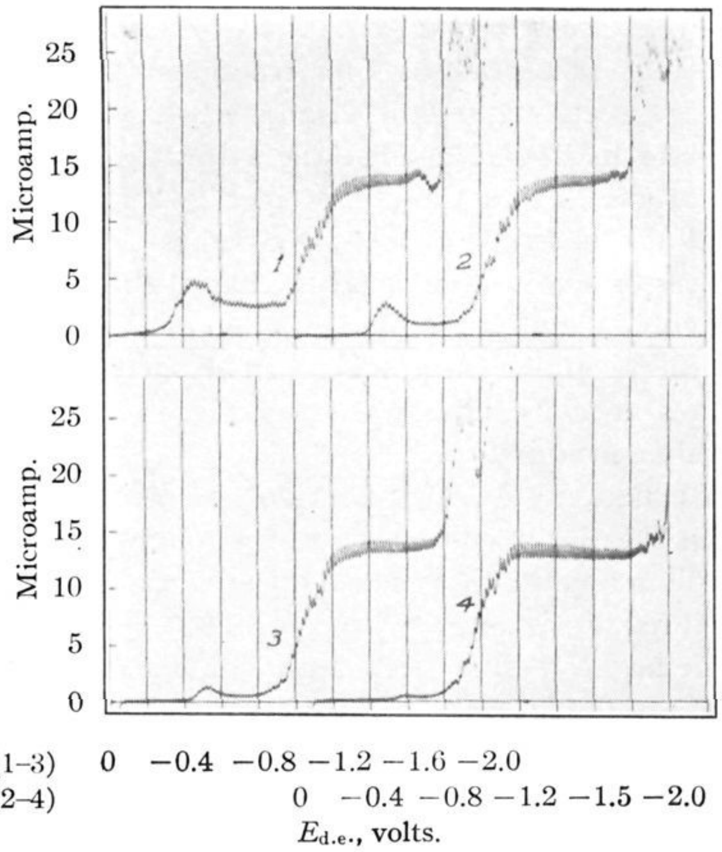

Fig. 1.—Current–voltage curves of 1.42×10^{-3} M potassium chromate in 0.1 N potassium chloride with various concentrations of sodium hydroxide: (1) no NaOH, (2) 0.002 N NaOH, (3) 0.013 N NaOH, (4) 0.2 N NaOH.

(In this and following polarograms, $E_{d.e.}$ signifies the potential of the dropping electrode against the saturated calomel electrode.) Addition of small amounts of sodium hydroxide to the solution decreases the first wave at −0.3 v., and it finally disappears when the concentration of sodium hydroxide is greater than about 0.2 N.

It will be noted that the height of the second wave at −1.0 v. is unaffected by the addition of sodium hydroxide, but the third ill-defined wave at −1.8 v. is, like the first wave, eliminated in 0.2 N sodium hydroxide.

C. v. curves of various concentrations of potassium chromate in 1 N sodium hydroxide as supporting electrolyte are shown in Fig. 2, and the corresponding values of the diffusion currents are given in Table I. The diffusion currents recorded in Table I have been corrected for the residual current that was obtained with the 1 N sodium hydroxide solution alone[1,4] (curve 1 in Fig. 2).

It will be noted that only one wave is obtained in 1 N sodium hydroxide solution, whose half-wave potential is at −0.85 v. *vs.* the S. C. E. The half-wave potential is practically constant and independent of the chromate concentration. The diffusion current is directly proportional to the concentration of chromate ions, as shown by the satisfactory constancy of the ratio i_d/C given in the last column of Table I.

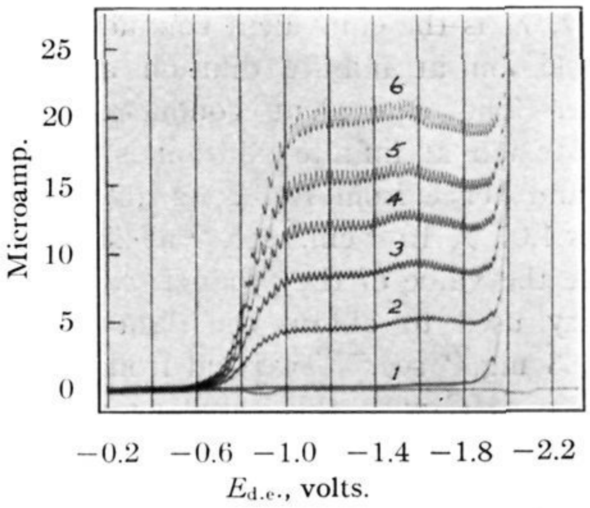

Fig. 2.—Various concentrations of potassium chromate in 1 N sodium hydroxide (see Table I).

TABLE I

RELATION BETWEEN THE DIFFUSION CURRENT AND THE CONCENTRATION OF CHROMATE IONS IN 1 N SODIUM HYDROXIDE

Diffusion currents measured at $E_{d.e.} = -1.2$ to -1.4 v. (see Fig. 2). $h = 72.1$ cm.; $m = 1.54$ mg. sec.$^{-1}$; $t = 3.36$ sec.; and $m^{2/3}t^{1/6} = 1.63$ mg.$^{2/3}$ sec.$^{-1/2}$ at $E_{d.e.} = -1.2$ v.

K_2CrO_4, millimoles per liter	i_d,[a] microamp.	i_d/C, microamp. per m mole per liter
0.473	4.35	9.20
0.901	8.40	9.33
1.298	12.00	9.25
1.667	15.52	9.32
2.100	20.08	9.55
		Av. 9.33 ± 0.09
	Calcd. for $n = 3$ (Eq. 3)	9.66

[a] Corrected for the residual current.

According to the Ilkovic equation the diffusion current should be given by[1,4]

$$i_d = 605nCD^{1/2}m^{2/3}t^{1/6} \text{ (microamperes)} \qquad (1)$$

where n is the number of faradays of electricity required per mole for the reduction, C is the concentration of the reducible substance in millimoles per liter, t is the drop time in sec., and D is the diffusion coefficient of the reducible substance in the units cm.^{2} sec.$^{-1}$. The general validity of this equation has been demonstrated in previous papers,[1,4] and it has also been shown that the effective diffusion coefficient of a reducible ion in the presence of an excess of supporting electrolyte can be calculated with satisfactory accuracy from the relation

$$D = \frac{RT\,\lambda_i^0}{zF_y^2} = 2.67 \times 10^{-7}\,\frac{\lambda_i^0}{z} \text{ (cm.}^2\text{ sec.}^{-1}) \qquad (2)$$

where R, T, and F_y are, respectively, the molar gas constant, the absolute temperature, and the faraday, λ_i^0 is the equivalent conductance of the reducible ion at infinite dilution and z is its valence. The equivalent conductance of the chromate ion at infinite dilution is 80.0 ohm^{-1} cm.^{2}, and hence from Eq. 2 its diffusion coefficient is 1.07×10^{-5} cm.^{2} sec.$^{-1}$ at 25°.

Since the value of the product $m^{2/3}t^{1/6}$ for the capillary used to obtain the data in Table I was 1.63 mg.$^{2/3}$ sec.$^{-1/2}$ we find from Eq. 1 that the ratio i_d/C with this capillary should be a function of n according to

$$i_d/C = 3.22\ n \qquad (3)$$

The observed value of i_d/C from the data in Table I is 9.33 microamp. per millimole per liter, corresponding to $n = 3$. Hence in alkaline medium the reduction of $CrO_4^{=}$ ions at the dropping electrode takes place according to

$$CrO_4^{=} + 4H_2O + 3e \longrightarrow Cr(OH)_3 + 5OH^- \qquad (4a)$$

or

$$CrO_4^{=} + 2H_2O + 3e \longrightarrow CrO_2^- + 4OH^- \qquad (4b)$$

the latter reaction predominating in strongly alkaline medium in which the solubility of $Cr(OH)_3$ is appreciable.[5]

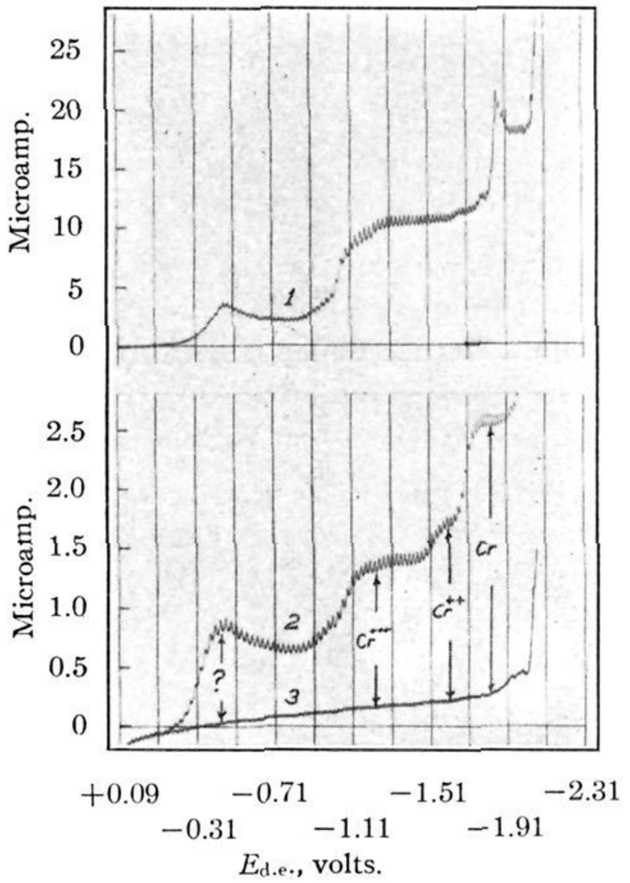

Fig. 3.—Increase of the relative height of the first wave with decreasing concentration of chromate in neutral unbuffered medium: (1) 1.10×10^{-3} M K_2CrO_4 in 0.1 N potassium chloride; (2) 1.19×10^{-4} M K_2CrO_4 in 0.1 N KCl; (3) residual current of 0.1 N KCl alone (see Table II).

From the free energy data listed by Latimer[6] the reversible potentials for reactions 4a and 4b are, respectively, −0.37 v. and −0.42 v. in 1 N sodium hydroxide against the saturated calomel electrode. From the curves in Fig. 2 it is seen that the observed reduction potential is several tenths of a volt more negative than the reversible potentials, and hence the reduction of $CrO_4^{=}$ ions at the dropping electrode is irreversible and requires a considerable overvoltage in strongly alkaline medium.

Reduction of $CrO_4^{=}$ does not proceed farther than the +3 oxidation state in strongly alkaline medium apparently because the potential actually required for $CrO_2^- \longrightarrow Cr^{+2}$, or $CrO_2^- \longrightarrow Cr^{\circ}$, is more negative than the potential at which sodium ions are discharged.

Reduction of Chromate in Unbuffered Solutions.—It was thought at first that the first wave at −0.3 v. in unbuffered solutions of potassium chloride as supporting electrolyte might be due to the reduction of $CrO_4^{=}$ ions to some oxidation state between +6 and +3. However, this hypothesis is invalidated by the fact that *the relative height of the first wave in unbuffered medium increases markedly with decreasing concentration of chromate.* This is demonstrated by the polarograms in Fig. 3, and the diffusion current data in Table II.

TABLE II

DIFFUSION CURRENTS OF THE THREE WAVES OF CHROMATE IN UNBUFFERED 0.1 N POTASSIUM CHLORIDE SOLUTION AS A FUNCTION OF THE CHROMATE CONCENTRATION

The three diffusion currents were measured at potentials of −0.8 v., −1.4 v., and −1.9 v., respectively (see Fig. 3). $h = 72.0$ cm., $m = 1.58$ mg. sec.$^{-1}$, and $m^{2/3}t^{1/6}$ was equal to 1.71, 1.66, and 1.60 mg.$^{2/3}t^{-1/2}$ at the foregoing three potentials.

K_2CrO_4, millimoles per liter	i_d, microamp.[a] at voltages			i_d/C, microamp. per m mole. per liter at voltages		
	−0.8	−1.4	−1.9	−0.8	−1.4	−1.9
0.016	0.11	0.15	0.32	6.9	9.4	20.0
.047	.28	.47	.91	6.0	10.0	19.4
.119	.55	1.23	2.32	4.6	10.3	19.5
.236	.88	2.36	4.34	3.7	10.0	18.4
.439	1.30	4.48	8.07	3.0	10.2	18.4
.736	1.68	7.40	[b]	2.3	10.1	
1.10	2.06	10.45	[b]	1.9	9.5	
1.42	2.40	13.35	[b]	1.7	9.4	
			Av.	...	9.86	19.2
	Calcd. for $n = 3$				9.90	
	Calcd. for $n = 6$					19.0

[a] Corrected for the residual current.

[b] Maxima present and diffusion current not well defined.

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[5] R. Fricke and O. Windhausen, *Z. anorg. allgem chem.*, **132**, 273 (1924).

[6] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938.

With concentrations of chromate smaller than 0.001 molar the last wave at −1.8 v. becomes well-defined (compare curve 1 of Fig. 1 with curve 2 of Fig. 3). It will be shown later that this last wave is due to the complete reduction of chromate ions to metallic chromium.

With concentrations of chromate less than about 2×10^{-4} M a fourth wave appears at −1.5 v. (curve 2, Fig. 3). The total diffusion current at −1.6 v. is very close to 4/3 the diffusion current at −1.3 v., and hence it corresponds to the reduction of chromate ion to chromous hydroxide according to

$$CrO_4^{=} + 4e + 4H_2O \longrightarrow Cr(OH)_2 + 6OH^- \qquad (5)$$

This same conclusion follows by application of the Ilkovic equation. The value of m for the capillary used to obtain the curves of Fig. 3 was 1.58 mg. sec.$^{-1}$ and t was equal to 3.00 sec. at $E_{\text{d.e.}} = -1.6$ v. Hence the product $m^{2/3}t^{1/6}$ was 1.63 mg.$^{2/3}$sec.$^{-1/2}$, and from Equations (1), (2) and (3) the calculated ratio of i_d/C for $n = 4$ is 12.9 microamp. The concentration of chromate used to obtain curve 2 of Fig. 3 was 0.119 mmoles per liter and the observed (corrected) diffusion current was 1.50 microamp. Hence the observed ratio of i_d/C is $1.50/0.119 = 12.6$ microamp., in good agreement with the calculated value for $n = 4$.

In Table II are listed the data obtained for the diffusion currents, corresponding to the three waves at −0.3 v., −1.0 v., and −1.8 v., of various concentrations of potassium chromate in unbuffered 0.1 N potassium chloride solution. The diffusion currents have been corrected for the residual current obtained with the 0.1 N potassium chloride solution alone.[1,4] The observed ratios of i_d/C for each of the three waves are listed in the last three columns, and the values of this ratio calculated from Eq. 1 for $n = 3$ and $n = 6$, respectively, are given at the bottom of the last two columns.

It will be noted that the diffusion currents of the second and last waves are directly proportional to the concentration of chromate, and the average values of i_d/C correspond very closely to values for n of 3 and 6, respectively. Hence the second wave is due to the reduction $CrO_4^{=} \longrightarrow Cr(OH)_3$, as in alkaline medium (Eq. 4), and the last wave corresponds to the complete reduction of $CrO_4^{=}$ ions to metallic chromium, according to the equation

$$CrO_4^{=} + 6e + 4H_2O \longrightarrow Cr^0 + 8OH^- \qquad (6)$$

It will be noted that the ratio of i_d/C for the first wave was not constant, but increased with decreasing concentration of chromate. It should also be mentioned that the peculiar rounded maximum shown by the first wave was neither suppressed by methyl red nor by gelatin. It is evident, from this fact, that the maximum is not a typical "adsorption" maximum,[1] but is due to some other cause.

In 1 N potassium chloride solution the first wave is well defined and does not show a maximum. However, just as in 0.1 N potassium chloride solution, the relative height of the first wave increases markedly with decreasing concentration of chromate.

When a relatively small concentration of a magnesium salt is added to a chromate solution in 0.1 N potassium chloride, the c. v. curve shows only a single wave starting at about −0.3 v., but the diffusion current is not well defined and it increases continuously with increasing applied e. m. f. This peculiar effect of magnesium ions is demonstrated in Fig. 4.

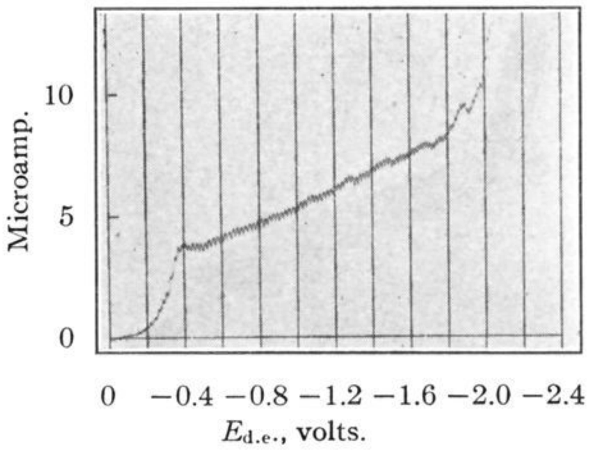

Fig. 4.—Influence of magnesium ions on the c. v. curve of chromate: 1.10×10^{-3} M K_2CrO_4 in 0.1 N KCl plus 0.01 M $MgCl_2$.

Reduction of Chromate in Buffered Solutions.—Typical c. v. curves of chromate reduction in two ammonia–ammonium chloride buffers of the same pH (8.7) but of different buffer capacity are shown in Fig. 5. Curve 1 was obtained with a 0.005 N and curve 2 with a 0.05 N buffer, and an excess of potassium chloride (0.1 N) was present in both cases. The most pronounced effect of the buffer was that it caused the first and second waves to coalesce into a single wave at −0.2 v. In the more concentrated buffer, the height of this wave corresponds to an n-value of 3 and hence reduction of chromate to chromic ions. The last wave at −1.6 v.

corresponds to the reduction of chromate ions to metallic chromium, as shown by the fact that the diffusion current corresponds to the value calculated from the Ilkovic equation for $n = 6$.

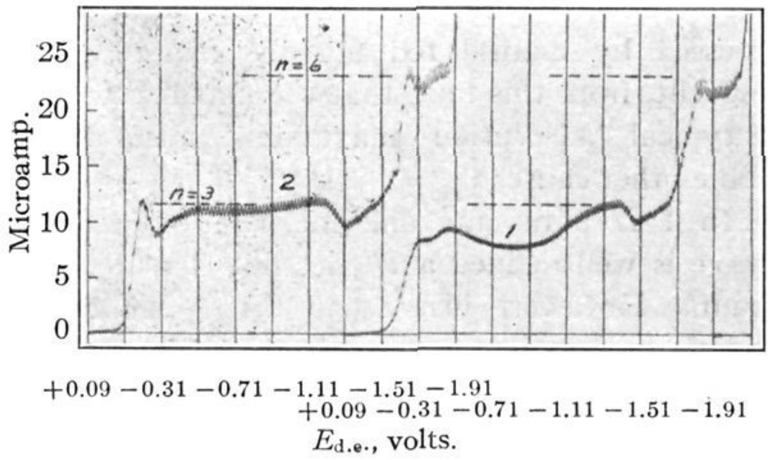

Fig. 5.—1.21×10^{-3} *M* K_2CrO_4 in 0.1 *N* KCl plus (1) 0.005 *N* NH_4Cl–NH_4OH buffer of *p*H 8.7, (2) 0.05 *N* NH_4Cl–NH_4OH buffer of *p*H 8.7. The short horizontal dotted lines indicate the diffusion currents calculated from the Ilkovic equation for values of *n* of 3 and 6, respectively.

From Eq. 4 it is evident that the concentration of hydroxyl ions formed at the electrode surface by the reduction will be between four and five times larger than the chromate ion concentration, depending on whether CrO_2^- or $Cr(OH)_3$ is formed. Hence in the reduction of the 1.21×10^{-3} *M* chromate solution, the concentration of hydroxyl ions liberated at the electrode surface was between about 0.005 and 0.006 *N*, when the diffusion current was reached. With the most dilute ammonium chloride–ammonia buffer (0.005 *N*, curve 1) the buffer capacity was not great enough to prevent a considerable change in the *p*H at the electrode surface, and this accounts for the fact that curve 1 has a shape intermediate between that of a c. v. curve in a completely unbuffered potassium chloride solution (compare Fig. 3) and that in a well-buffered ammonium chloride–ammonia solution. There was no significant change in the shape of the c. v. curve with increasing concentration of the ammonium chloride–ammonia buffer between 0.05 and 1 *N*.

The characteristics of the c. v. curve were also practically the same in various ammonia–ammonium chloride buffers of constant ammonium chloride concentration (0.1 *N*) but of different *p*H values between about 7.5 and 10. The reduction potential of the first wave was only shifted by a few hundredths of a volt, from −0.10 to −0.17 v., when the *p*H of a 0.1 *N* ammonium chloride–ammonia buffer was varied from 8 to 10. C. v. curves of 0.001 molar potassium chromate in 0.1 *N* ammonium chloride as supporting electrolyte (*p*H about 5) were similar to curve 2 in Fig. 5, except, as was to be expected, the reduction began at a more positive potential (+0.1 v.) and the slope of the first wave was smaller. The smaller slope was undoubtedly due to the poor buffer capacity of the pure ammonium chloride solution, and the consequent change in *p*H at the electrode surface with increasing current.

We also investigated the effect of diethylammonium chloride–diethylammonium hydroxide buffers of various *p*H values. Since the dissociation constant of diethylamine, 1.3×10^{-3}, is about one hundred times larger than that of ammonia it was possible to study the c. v. curves in these buffers up to a *p*H of about 12, and compare the characteristics of the curves with those obtained in dilute (*ca.* 0.01 *N*) sodium hydroxide solutions of about the same *p*H. The characteristics of the c. v. curve of chromate in a 0.1 *M* diethylammonium chloride–diethylammonium hydroxide buffer at a *p*H of about 10 are practically the same as those in an ammonium chloride–ammonia buffer of the same *p*H. At a *p*H of 10 only two waves were obtained at −0.35 v. and −1.8 v., as shown in Fig. 6. However, as the *p*H was shifted from 10 to 12 the reduction potential of the first wave ($CrO_4^{=} \longrightarrow Cr^{+++}$) was shifted markedly from −0.35 v. to −1.1 v., and the second wave at −1.8 v. ($CrO_4^{=} \longrightarrow Cr$) disappeared at a *p*H of 12. At a *p*H of 12 in a diethylammonium chloride–diethylamine buffer the c. v. curve showed only a single wave which closely resembled the single wave in dilute solutions of sodium hydroxide, both in the magnitude

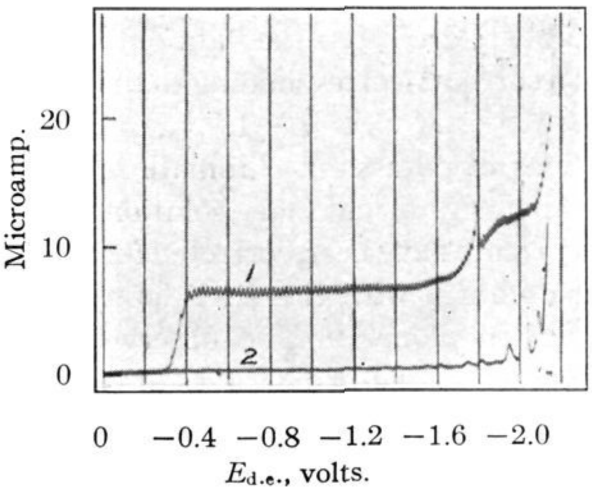

Fig. 6.—(1) 7×10^{-4} *M* potassium chromate in 0.1 *M* diethylammonium chloride–diethylamine buffer of *p*H 10.2. (2) Residual current of buffer alone.

of the diffusion current and the value of the reduction potential. There was also a slight indication of a "pre-wave" in the diethylammonium chloride–diethylamine buffers of *p*H 11 and 12, just as in the dilute sodium hydroxide solutions.

In a 0.1 N solution of borax in 0.1 N potassium chloride (*p*H about 9) only a single well-defined wave was obtained at −0.3 v., and the diffusion current corresponded to $CrO_4^{=} \longrightarrow Cr^{+++}$. There was some indication of a second wave at −1.8 v., about twice as large as the first wave, but it was not well defined.

Discussion

The most interesting phenomenon observed in the reduction of chromate at the dropping electrode is the first wave at −0.3 v. in unbuffered solutions (Fig. 1 and Fig. 3). The most logical explanation of this wave appears to be that it is due to the reduction of $CrO_4^{=}$ ions, but that its height does not correspond to $n = 3$ because of the formation of a film of either chromic hydroxide, or basic chromic chromate, at the electrode surface which interferes with the further reduction.

The formation of basic chromic chromate at solid cathodes, presumably as a stable film impervious to chromate ions, is the usual explanation given to account for the low current efficiency in technical chromium plating.[7] According to Müller and Ekwall[8] the formula of the chromic chromate precipitated at a platinum or carbon cathode is $Cr_2(OH)_4CrO_4$, or $Cr(OH)_3 \cdot CrOH\text{-}CrO_4$. A variety of different "chromic chromates" probably can be formed depending on the experimental conditions, particularly the *p*H at the electrode surface.

Quantitative interpretation of the first wave in the present experiments, and the effect of *p*H on the reduction potential, is not possible at the present time because the detailed mechanism of the reduction is unknown. In this connection it should be emphasized that Equations 4a and 4b are intended to represent merely the *net* reaction, and not the actual mechanism of the reduction.

Qualitatively, however, the observed effects indicate that the formation of a film on the surface of the mercury drops increases the overvoltage necessary to obtain complete reduction of $CrO_4^{=}$ to Cr^{+3}. In neutral unbuffered solutions complete reduction to the +3 state does not start until a potential of about −1.0 v. is reached. When sodium hydroxide is added to the solution the first wave is decreased and shifted to a more negative value, but the second wave ($CrO_4^{=} \longrightarrow Cr^{+3}$) is shifted to a more positive value, and in 1 N sodium hydroxide solution it starts at about −0.7 v. (Fig. 1 and Fig. 2). Apparently the film of basic salt is not formed in strongly alkaline solution, because the chromic chromium remains in solution as chromite ion (CrO_2^-).

There seems to be a critical range of hydroxyl ion concentration in which the film formation occurs, which is to be expected from the amphoteric nature of the chromic ion. Apparently the film does not form in buffer solutions of *p*H less than 10 or 10.5, since in such solutions the height of the wave corresponds to $n = 3$. Under the present experimental conditions, the film appears to be stable only over a *p*H range from about 10.5 to 13 or 13.5.

In alkaline buffers the reduction potential shifts to more negative values with increasing *p*H, but the interpretation of the shift is complicated by the fact that it depends on the kind of buffer used as well as on the *p*H.

Summary

The reduction of chromate at the dropping electrode has been investigated in neutral unbuffered solutions, in buffer solutions of *p*H between 8 and 12, and in strongly alkaline medium.

With 1 N sodium hydroxide as supporting electrolyte the current–voltage curve consists of only a single well-defined wave, with a half wave potential of −0.85 v. *vs.* the saturated calomel electrode which is independent of the concentration of chromate. The height of the wave, which is directly proportional to the chromate concentration, corresponds to the reduction of $CrO_4^{=}$ to the +3 oxidation state (CrO_2^- in strongly alkaline medium).

In unbuffered solutions of potassium chloride the c. v. curve consists of four distinct waves at −0.3 v., − 1.0 v., −1.55 v., and −1.8 v., *vs.* the S. C. E. It was shown that the last three waves correspond, respectively, to $CrO_4^{=} \longrightarrow Cr^{+3}$, $CrO_4^{=} \longrightarrow Cr^{+2}$, and $CrO_4^{=} \longrightarrow Cr$. From the fact that the *relative* height of the first wave at −0.3 v. increased markedly with decreasing concentration of chromate, it was concluded that this wave was not due to the reduction of

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[7] S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction," D. Van Nostrand Co., Inc., New York, 1936, p. 120.

[8] E. Müller and P. Ekwall, *Z. Elektrochem.*, **35**, 84 (1929).

$CrO_4^=$ to some oxidation state between +6 and +3, but that the limiting current is governed by the formation of a film of chromic hydroxide, or basic chromic chromate, at the electrode surface, which interfered with the further reduction. When the solution was well-buffered at a *p*H between 8 and 10 the diffusion current at −0.3 to −0.4 v. corresponded to the reduction $CrO_4^= \longrightarrow Cr(OH)_3$. Apparently the film of basic salt is only stable under the conditions of the present experiments over a *p*H range from about 10.5 to 13.5.

From an analytical viewpoint, 1 *N* sodium hydroxide is the most suitable supporting electrolyte for the polarographic determination of chromate.

BERKELEY, CALIFORNIA
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 10, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Ternary Systems. XXIV. Some Further Solid Solutions of Alums, at 25°[1]

BY ARTHUR E. HILL, NORMAN O. SMITH AND JOHN E. RICCI

This is a report of experiments continuing an investigation, conducted in this Laboratory, of ternary systems involving the formation of solid solutions between isomorphous double salts in equilibrium with aqueous solution. The general purpose of the investigation is the accumulation of reliable data on which to base, ultimately, speculations on the formation of solid solutions between such salts. In this respect it has been of interest especially to study the distribution of the two salts between the conjugate liquid and solid solutions, and to attempt to relate this distribution with the aqueous solubilities of the individual salts. On the basis of results, already published, on the formation of such solid solutions in a series of picromerites, studied as ternary systems of pairs of double salts with water,[2a] and in a number of alum pairs,[2b] an empirical equation has already been suggested[2a] for the relation between the mole fraction of a component in the liquid phase and its mole fraction in the solid phase; the degree of success toward a theoretical interpretation of the observed relation will be presented in a forthcoming publication from this Laboratory, making use of the present and additional data collected on this type of system.

Alums crystallize as regular octahedra and provided the lattice dimensions be not greatly different they would be expected to form solid solutions with one another. Early work with alums had been done by Hollmann[3] with the alum pairs $KFe(SO_4)_2$–$KAl(SO_4)_2$ and $KCr(SO_4)_2$–$KAl(SO_4)_2$, and by Fock[4] with the pair $KAl(SO_4)_2$–$TlAl(SO_4)_2$. In addition Hill and Kaplan[2] have studied the pairs $NH_4Al(SO_4)_2$–$KAl(SO_4)_2$, $NH_4Fe(SO_4)_2$–$NH_4Al(SO_4)_2$ and $NH_4Al(SO_4)_2$–$NaAl(SO_4)_2$. Complete miscibility between the alums was found in all these pairs studied, with the exception of the last mentioned, the sodium alum–ammonium alum pair, which formed no solid solution at all at the temperature of the measurements, 25°. The present paper describes similar measurements for the following pairs of alums in equilibrium with aqueous solutions at 25°: $TlAl(SO_4)_2$–$NH_4Al(SO_4)_2$, $TlAl(SO_4)_2$–$KAl(SO_4)_2$, $NH_4Cr(SO_4)_2$–$KCr(SO_4)_2$ and (partially) the pair $NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$; complete miscibility was found to prevail for all these pairs at the temperature studied. Included also in this report is the ternary system for the formation of thallium alum from its component salts and water at 25°. This was desirable in view of the fact that thallium alum was to be prepared for use in solid solutions with other alums.

As has been emphasized in the preceding papers of this series, the present measurements are distinguished by the fact that special attention has been given to the question of attainment of equilibrium, inasmuch as the uncertainty about equilibrium generally vitiates the older results on the solubilities of such mixed salts. The procedure followed, for this purpose, already has been described,[2] the essential point being that

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[1] This paper is being published, following the death of Professor Hill, by his collaborators. The material of the article is taken from a thesis presented for the degree of Doctor of Philosophy at New York University, June, 1939, by N. O. Smith, whose present address is the University of Manitoba, St. Vital, Manitoba, Canada.

[2] (a) Hill and Taylor, THIS JOURNAL, **60**, 1099 (1938); (b) Hill and Kaplan, *ibid.*, **60**, 550 (1938).

[3] Hollmann, *Z. physik. Chem.*, **37**, 193 (1901).

[4] Fock, *Z. Krist.*, **28**, 337 (1897).