[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

The Potential of the Ag(s), Ag_2CrO_4(s), $CrO_4^=$ Electrode[1]

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The purpose of this investigation was to determine, by means of electromotive force measurements, the potential of the Ag(s), Ag_2CrO_4(s), $CrO_4{}^=$ electrode.

A search of the literature revealed that very little work had been done on this electrode.[2] No description of an electrolytic deposition of silver chromate could be found.

Method and Apparatus

In this investigation the cell Ag(s), Ag_2CrO_4(s), K_2CrO_4(aq), KCl(aq), AgCl(s), Ag(s) was measured. The apparatus used was suggested by the work of Randall and Cann.[3] The electrodes were placed in the outer arms of the electrode vessels so as to prevent the flow of liquid over the electrodes.[4]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

Materials

All solutions were made up by weight, moles per 1000 g. of water in vacuum, from high grade "analyzed" salts and conductivity water. Either pure hydrogen or nitrogen was bubbled through the solutions to remove traces of oxygen.

The Ag(s), AgCl(s) spiral electrodes were made according to the method of Randall and Young.[5]

The Ag(s), Ag_2CrO_4(s) spiral electrodes were also made electrolytically. Many trials showed that the best results were obtained with a 0.02 molal chromic acid solution using an e. m. f. of 1.5 volts for about two hours. A solution of chromic acid instead of potassium chromate was used to prevent contamination by the potassium ion. The electrodes were then washed in distilled water and short-circuited together for some hours. When not in use they were kept in a dilute solution of potassium chromate, for according to Margosches[6] the solubility of silver chromate is less in potassium chromate than in water. Immediately before being introduced into the cell the electrodes were placed in the particular potassium chromate solution to be used and evacuated for about thirty minutes, with gentle heating, to make sure of the complete removal of all oxygen.

Experimental Results

The molality of the potassium chloride was twice that of the potassium chromate in order to have the same concentrations of potassium ions in the two solutions. This is necessary for the Lewis and Sargent[7] formula for liquid junction potentials. Table I gives the average values of at least ten cell readings for each concentration used. The readings in general did not vary from the average by more than ±0.5 millivolt, except in the most dilute solutions, where the maximum variation was ±1.0 millivolt.

TABLE I

Molality of K_2CrO_4	Molality of KCl	E. m. f. at 25°C. v.	Liquid junction π, v.	E. m. f. $-\pi$, v.	E. m. f. Ag, AgCl, v.	E. m. f. Ag, Ag_2,CrO_4, v.
0.100	0.200	−0.2223	0.0036	−0.2259	0.2709	−0.4968
.050	.100	− .2152	.0026	− .2178	.2872	− .5050
.025	.050	− .2078	.0019	− .2097	.3035	− .5132
.010	.020	− .1876	.0010	− .1886	.3255	− .5141
.005	.010	− .1784	.0005	− .1789	.3425	− .5214
.00375	.0075	− .1726	.0003	− .1729	.3494	− .5223
.0025	.0050	− .1659	.0001	− .1660	.3596	− .5256

The liquid junction potential was calculated for each concentration by using the Lewis and Sargent[7] formula for common cations, *i. e.*

$$E = -\frac{RT}{F} \ln \Lambda_{\mathrm{KCl}}/\Lambda_{1/2\mathrm{K_2CrO_4}}$$

The values for the individual ion conductances were taken from the "International Critical Tables."[8]

In order to determine the potential of the silver–silver chromate electrode from the cell readings, it is necessary to know the potential of the silver–silver chloride electrode for each dilution used. Since both silver and silver chloride

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[1] The experimental part of this paper is a portion of a thesis submitted by G. B. Mueller in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

[2] Abegg and Cox, *Z. physik. Chem.*, **46**, 1 (1904); Bolam and MacKenzie, *Trans. Faraday Soc.*, **22**, 162 (1904); *C. A.*, **20**, 2772 (1926); *Trans. Faraday Soc.*, Advance Proof; Hass and Jellinek, *Z. physik. Chem.*, **162**, 153 (1932).

[3] Randall and Cann, THIS JOURNAL, **52**, 589 (1930).

[4] Carmody, *ibid.*, **54**, 210 (1932); Cann and LaRue, *ibid.*, **54**, 3456 (1932).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Margosches, *Z. anorg. Chem.*, **51**, 231 (1906).

[7] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[8] "International Critical Tables," McGraw-Hill-Book Co., Inc., New York City, 1930, Vol. VI, pp. 234, 253.

are solids, this value is calculated for each concentration by means of the equation

$$E = E^0 - (RT/F) \ln (m\gamma)_{Cl^-}$$

and since it is generally assumed that the activity coefficients of the potassium and chloride ions are equal, the activity coefficients of potassium chloride may be used for those of the chloride ion. These values were taken from Lewis and Randall.[9]

The value of E^0 for the silver–silver chromate electrode was calculated from the values listed in Table I. Since the electrode reaction is

$$2Ag(s) + CrO_4^{=} \longrightarrow Ag_2CrO_4(s) + 2e$$

we may write

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{a_{CrO_4^{=}}} = E^0 - \frac{RT}{2F} \ln \frac{1}{(m\gamma)_{CrO_4^{=}}}$$

By subtraction of $(RT/2F) \ln m$ from both sides of the equation

$$E - \frac{RT}{2F} \ln m = E^0 - \frac{RT}{2F} \ln \frac{1}{\gamma_{CrO_4^{=}}}$$

At infinite dilution the activity coefficient is equal to one, and the last term drops out; thus

$$E - (RT/2F) \ln m = E^0$$

We therefore determine E^0 by plotting $(E - (RT/2F) \ln m)$, *i. e.*, $E - 0.02958 \log m$ against the molality and extrapolating the curve to infinite dilution. The values so determined are given in Table II. From the plot of these values E^0 was taken as -0.4463 v. This gives $\Delta F^0 =$ 20,596 cal.

TABLE II

Molality of K_2CrO_4	E. m. f., v.	0.02958 log *m*, v.	E. m. f. −0.02958 log *m*, v.	C. & M. $\gamma_{CrO_4^{=}}$	H. & J. $\gamma_{CrO_4^{=}}$
0.50					0.14
.10	−0.4968	−0.0296	−0.4672	0.19	.24
.05	− .5050	− .0394	− .4656	.21	.28
.025	− .5132	− .0474	− .4658	.32	
.010	− .5141	− .0592	− .4549	.51	.465
.005	− .5214	− .0681	− .4533	.64	.54
.00375	− .5223	− .0718	− .4505	.72	
.0025	− .5256	− .0770	− .4476	.83	

Combining

$$2Ag(s) + CrO_4^{=} \longrightarrow Ag_2CrO_4(s) + 2e; \quad \Delta F^0 = 20{,}596$$

and

$$2Ag(s) \longrightarrow 2Ag^+ + 2e; \quad \Delta F^0 = 36{,}896$$

we have

$$2Ag^+ + CrO_4^{=} \longrightarrow Ag_2CrO_4(s); \quad \Delta F^0 = -16{,}300 \text{ cal.}$$

The activity coefficients of the chromate ion were calculated by the equation

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{(m\gamma)_{CrO_4^{=}}}$$

The temperature coefficient was determined for the cell containing 0.05 *M* KCl and 0.025 *M* K_2CrO_4. The values listed in Table III are the averages of at least five readings at each temperature. From the plot of these values $dE/dT = -0.000228$.

Hence, since

$$E + \frac{\Delta H}{nF} = T\frac{dE}{dT}$$

$\Delta H_{298.1}$ for the reaction was found to be 6225 cal.

TABLE III

°C	E. m. f., v.
14.8	−0.2102
25.0	− .2078
30.0	− .2069
35.0	− .2060
40.0	− .2044
45.0	− .2023

To obtain the heat of formation of silver chromate, we make the combinations

$$2AgCl(s) + CrO_4^{=} \longrightarrow Ag_2CrO_4 + 2Cl^-; \quad \Delta H^0 = 6225 \text{ cal.}$$

$$2Ag^0 + Cl_2 \longrightarrow 2AgCl; \quad \Delta H^0 = -60{,}540 \text{ cal.}^{10}$$

$$2Ag^0 + Cl_2 + CrO_4^{=} \longrightarrow Ag_2CrO_4 + 2Cl^-; \quad \Delta H^0 = -54{,}315 \text{ cal.}$$

$$Cl_2 \longrightarrow 2Cl^-; \quad \Delta H^0 = -79{,}166 \text{ cal.}^{11}$$

$$2Ag^0 + CrO_4^{=} \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = 24{,}851 \text{ cal.}$$

$$Cr^0 + 2O_2 \longrightarrow CrO_4^{=}; \quad \Delta H^0 = -203{,}952 \text{ cal.}^{12}$$

$$2Ag^0 + Cr^0 + 2O_2^0 \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = -179{,}101 \text{ cal.}$$

Thus the heat of formation of silver chromate from its elements is

$$\Delta H^0_{298.1} = -179{,}101 \text{ cal.}$$

It is also interesting to calculate the heat of formation of silver chromate from its ions. We combine

$$2Ag^0 + CrO_4^{=} \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = 24{,}851 \text{ cal.}$$

$$2Ag^0 \longrightarrow 2Ag^+; \quad \Delta H^0 = 49{,}724 \text{ cal.}^{13}$$

$$2Ag^+ + CrO_4^{=} \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = -24{,}873 \text{ cal.}$$

The entropy change for this reaction is obtained from

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

$$-16{,}300 = -24{,}873 - 298.1\ \Delta S^0$$

$$\Delta S^0_{298.1} = -28.75$$

Discussion of Results

Abegg and Cox[2] measured the cell

$Ag(s), Ag_2CrO_4(s), K_2CrO_4$ (0.1 *N*), KCl(*N*), Hg_2Cl_2, Hg

and found it to give an e. m. f. of -0.227 v. at

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, pp. 360, 362.

[10] Wolff, *Z. Elektrochem.*, **20**, 19 (1914); Jellinek and Uloth, *Z. physik. Chem.*, **119**, 161 (1926); Ref. 8, Vol. V, p. 188.

[11] Trautz and Geissler, *Z. anorg. allgem. Chem.*, **140**, 116 (1924); Ref. 8, Vol. V, p. 176.

[12] Ref. 8, Vol. V, p. 193.

[13] Ref. 8, Vol. V, p. 188.

25°. Using the value −0.2800 v.[5,14] for the normal calomel electrode, we obtain for Ag(s), Ag_2CrO_4(s), 0.1 *N* $CrO_4^=$ the value $E = -0.507$ v. This is in good agreement with our value of −0.5050 v. Next, calculating the value of E^0 from Abegg and Cox's results, we obtain −0.448 which again agrees with our value of −0.4463.

Bolam and MacKenzie[2] measured the cell Ag, $AgNO_3$(0.1 *N*), NH_4OH(10 *N*), K_2CrO_4(0.1 *N*), Ag_2CrO_4, Ag and obtained the value 0.2247 v. Lewis[15] found $E = -0.399$ v. for the cell Ag, $AgNO_3$(0.1 *M*), KNO_3(0.1 *M*), KCl(0.1 *M*) Hg_2Cl_2, Hg. Noyes and Brann[16] found for this same cell $E = -0.3992$ v. Lewis and Randall,[9] (p. 414) on the basis of these results, corrected for the liquid junction and obtained $E = -0.3985$ v. Since the value of the decinormal calomel electrode is −0.3351 v., we thus obtain for Ag(s), Ag_2CrO_4(s), CrO_4 = (0.1 *N*) the value $E = -0.5089$ v. This gives $E^0 = -0.4504$ v.

The standard electrode potential calculated from the data of Hass and Jellinek[2] is $E^0 = -0.462$ v.

The change in free energy for the reaction

$$Ag_2CrO_4(s) \longrightarrow 2Ag^+ + CrO_4^=$$

may be calculated from the solubility product as well as from the standard electrode potentials. Values calculated from various data are summarized in Table IV. Hass and Jellinek[2] measured the potential of the silver–silver chromate electrode in order to calculate the activity coefficients of the chromate ion. Their values, compared with ours, are listed in Table IV.

TABLE IV

Investigator	E^0, v.	*K* s. p.	ΔF^0 $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^=$ cal.
Hass and Jellinek[2]	−0.462		15,576
Bolam and MacKenzie[2]	− .4504		16,111
Abegg and Cox[2]	− .448		16,222
Cann and Mueller	− .4463		16,300
Abegg and Shäfer[a]		2.64×10^{-12}	15,803
Kohlrausch[b]		4.05×10^{-12}	15,550
Sherrill[c]		9.0×10^{-12}	15,077

[a] *Z. anorg. Chem.*, **45**, 293 (1905).

[b] *Z. physik. Chem.*, **64**, 149 (1908).

[c] THIS JOURNAL, **29**, 1641 (1907).

The variation in these values may be due to the fact that electrolytic silver chromate was used in the present work, whereas Hass and Jellinek used the precipitated salt. The thermodynamic properties of substances prepared by dissimilar methods may be very different.

Summary

The cell Ag(s), Ag_2CrO_4(s), K_2CrO_4(aq), KCl(aq), AgCl(s), Ag(s) was investigated.

The normal electrode potential of Ag(s), Ag_2CrO_4(s), $CrO_4^=$ was found to be $E^0 = -0.4463$ v.; $\Delta F^0 = 20{,}596$ cal.

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[14] Spencer, THIS JOURNAL, **54**, 3649 (1932).

[15] Lewis, *ibid.*, **28**, 158 (1906).

[16] Noyes and Brann, *ibid.*, **34**, 1016 (1912); Bray and Hershey, *ibid.*, **56**, 1891 (1934).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Adsorption of Hydrogen and Deuterium on Copper at Low Pressures[1]

BY RALPH A. BEEBE, GEORGE W. LOW, JR., EDWIN LINCOLN WILDNER AND SEYMORE GOLDWASSER

Attention has been called by Pace and Taylor[2] to the fundamental importance which is attached to experimental studies of the relative velocities of the activated adsorption of hydrogen and deuterium on catalytically active surfaces. These authors have found no difference in the rates of adsorption for the two isotopes on the hydrogenating catalysts chromium oxide, zinc oxide–chromium oxide and nickel at one atmosphere pressure and over the temperature range 110–184°. This observation was unexpected because, on account of the difference in zero point energies, the activation energy should be greater for deuterium than for hydrogen, and the rate of adsorption correspondingly less for deuterium.

More recently direct experimental evidence has been presented by Klar,[3] and indirect evidence based upon the interpretation of the rates of catalytic reactions has been presented independently by Klar,[4] and by Fajans[5] to show very definite differences in the adsorption of the two hydrogen isotopes on active nickel.

Because of the apparent discordance among the

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[1] Presented before the Division of Physical and Inorganic Chemistry at the ninety-first meeting of the American Chemical Society held in New York City on April 22–26, 1935.

[2] Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[3] R. Klar, *Naturwiss.*, **22**, 822 (1934).

[4] R. Klar, *Z. physik. Chem.*, **27B**, 319 (1935).

[5] E. Fajans, *ibid.*, **28B**, 239 (1935).