trend of the values based on experiment does not depend appreciably on the value selected for the temperature coefficient of the electronic contribution, but it does depend on the validity of extrapolating the Nernst–Grüneisen approximation for ($C_p - C_v$) to these higher temperatures. As stated previously, there is evidence both from thermal expansion data and electrical resistivity data that some sort of transition occurs in beryllium or its impurities in this temperature region. Whereas in Fig. 3 the values of C_p give some indication that there is such a change in this region, it is much more obvious from the deviations of the values of ($C_v - C_{\text{electronic}}$) from the Debye curve that the change in the material is real.

It is of interest as to what electronic contribution, if any, is shown by the specific heat of beryllium at very low temperatures. Such measurements of its specific heat have been made in the range from 10 to 300 °K. primarily for the express purpose of answering this question.[16] Disregarding a pronounced irregularity found in the variation with temperature up to approximately 15 °K., these workers deduced some systematic deviation of C_v from the T^3 law. However, they preferred to agree with other authors that this law is very likely to be inaccurate in the case of crystals of the type assumed by beryllium, and hence is incapable of being used for even an estimation of the electronic contribution. In fact, their specific-heat values cannot be assumed to follow the T^3 law and to contain as well more than a small fraction of the electronic contribution predicted from that indicated in Fig. 3. The available low-temperature evidence thus seems inconclusive.

The agreement is good between the values for ($C_v - C_{\text{electronic}}$) and the Debye curve between 300 and 800 °K., as shown in Fig. 3, and leads to a value of θ_D, the Debye temperature, of 930°. This value from the high-temperature measurements reported in this paper may be compared with the value of 1050° given by the low-temperature specific heat values between 20 and 60 °K. referred to above.[16]

WASHINGTON, D. C. RECEIVED OCTOBER 2, 1950

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[16] S. Critescu and F. Simon, *Z. physik. Chem.*, **B25**, 273 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Polarographic Study of Chromium(III) Chloride Solutions[1]

BY RANDALL E. HAMM AND CHARLES M. SHULL, JR.

Fresh solutions of chromium(III) chloride were found to be reduced at a half-wave potential of −0.61 v. *vs.* S.C.E., whereas aged solutions of this salt were reduced at a much more negative half-wave potential. This ambiguous new wave was found to decrease in height and disappear as the solution aged. It was assumed that the wave at −0.61 v. was due to reduction of $[CrCl_2(H_2O)_4]^+$, while that from the fully aged solution was due to reduction of hexaquochromium(III) ion. A study of this new wave was made using it as a method of following the first step of the transition of green to violet modification of chromium(III) chloride. The transition was found to be first order with respect to chromium and independent of the chloride concentration. The rate was proportional to the reciprocal of the hydrogen ion concentration. A rate equation was developed which showed this dependence upon hydrogen ion concentration, and was consistent with the equations usually given for the reaction. The temperature dependence of the rate of transition was studied and the activation energy calculated.

A complete investigation of the behavior of chromium(III) chloride when reduced at the dropping mercury electrode has never been reported, although Demassieux and Heyrovsky,[2] Prajzler,[3] and Lingane and Pecsok[4] have reported on the reduction of chromium(III) chloride in aged solutions. None of these investigators have reported on the results with fresh solutions or on any attempt to follow the aging process at the dropping mercury electrode, although Demassieux and Heyrovsky[2] did make the observation that concentrated solutions were more easily reduced and attributed this, correctly, to the presence of $[CrCl_2(H_2O)_4]^+$ in the concentrated solutions.

Many workers[5-9] have made investigations of the chemistry of chromium(III) chloride solutions, but there is still some discussion of the changes taking place in solution. It is the purpose of this paper to present the behavior of fresh chromium(III) chloride solutions at the dropping mercury electrode and to contribute to the studies of the chemistry of trivalent chromium solutions.

The transition from green to violet chromic chloride has been followed by Bjerrum[7a] and Lamb and Fonda,[9] by means of the change of conductance of solutions of green chromic chloride solutions. The data taken in this manner were difficult to interpret because of the simultaneous change of conductance caused by different degrees of hydrolysis of the various ionic species, and because the transition is essentially two consecutive steps. These difficulties did not seriously interfere in the polarographic method since it was found that the original green form was reduced at a potential sufficiently different that the change in concentration of the green form could be followed.

Pfeiffer[10] originally, without experimental data, proposed reactions for the transition according to the usual Werner scheme. The following represent the transitions that occur in a fresh chromium(III) chloride solution. They are consistent with the

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[1] Presented before the Annual Meeting of the Pacific Division of the American Association for the Advancement of Science held in Salt Lake City, Utah, June 19 to 24, 1950.

[2] N. Demassieux and J. Heyrovsky, *J. chim. phys.*, **26**, 219 (1929).

[3] J. Prajzler, *Collection Czechoslov. Chem. Commun.*, **3**, 406 (1931).

[4] J. J. Lingane and R. L. Pecsok, THIS JOURNAL, **71**, 425 (1949).

[5] A. B. Lamb, *ibid.*, **28**, 1710 (1906).

[6] J. Olie, *Z. anorg. Chem.*, **51**, 29 (1907); **53**, 268 (1908).

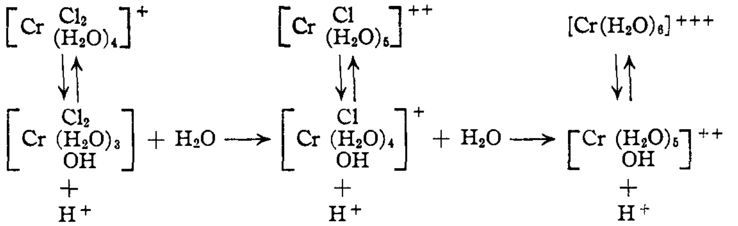
[7] (a) N. Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907); (b) **73**, 724 (1910).

[8] A. Heydweiller, *Z. anorg. Chem.*, **91**, 66 (1915).

[9] A. B. Lamb and G. R. Fonda, THIS JOURNAL, **43**, 1154 (1921).

[10] P. Pfeiffer, *Ber.*, **34**, 2559 (1901).

kinetics that were found in this investigation and are similar to those proposed by Pfeiffer.



$$\begin{array}{ccccc}
[\mathrm{Cr}\,\mathrm{Cl_2}(\mathrm{H_2O})_4]^{+} & & [\mathrm{Cr}\,\mathrm{Cl}(\mathrm{H_2O})_5]^{++} & & [\mathrm{Cr(H_2O)_6}]^{+++} \\
\downarrow\uparrow & & \downarrow\uparrow & & \downarrow\uparrow \\
[\mathrm{Cr}\,\mathrm{Cl_2}(\mathrm{H_2O})_3\mathrm{OH}] & + \mathrm{H_2O} \longrightarrow & [\mathrm{Cr}\,\mathrm{Cl}(\mathrm{H_2O})_4\mathrm{OH}]^{+} & + \mathrm{H_2O} \longrightarrow & [\mathrm{Cr}(\mathrm{H_2O})_5\mathrm{OH}]^{++} \\
+ & & + & & + \\
\mathrm{H^+} & & \mathrm{H^+} & & \mathrm{H^+}
\end{array} \qquad (1)$$

Experimental

Apparatus and Materials.—The polarograph used for all measurements was a Sargent model XII polarograph. When this was used for rate determinations the slide wire was carefully set at −0.71 v. *vs.* S.C.E. and the camera disengaged from the slide wire. Measurements were recorded after turning the camera manually for each time interval desired. The photographic record was developed and the average diffusion current for each recorded point measured to ±0.5 mm. or better.

The cell was an H type cell with a saturated calomel electrode in one branch, a saturated potassium chloride–agar gel in the cross member and the solution being investigated in the remaining branch. The dropping mercury electrode was a piece of marine barometer tubing 7 cm. long which had the following characteristics at 25°, as determined from time to time by the method of Lingane[11]: m = 2.503 mg./sec., t = 2.75 sec./drop in 0.1 molar potassium chloride at a potential of one volt *vs.* S.C.E.

Merck & Co., Inc., Reagent chromium chloride was used for preparing solutions of chromium(III) chloride. The potassium chloride was of reagent grade. The sodium perchlorate used was prepared by neutralization of pure perchloric acid with carbonate free sodium hydroxide as described by Lingane and Pecsok.[4]

The *p*H of the solutions was determined with a Beckman model G *p*H-meter, which was calibrated against 0.05 molar potassium acid phthalate.

Procedure.—The solutions were prepared by weighing out the chromium chloride and adding it, potassium chloride, hydrochloric acid and gelatin to a 500-ml. volumetric flask and diluting to the mark. All measurements were made on solutions containing about 0.001% gelatin as a maximum suppressor. Since the *p*H of solution changed as the aging process took place, best results were obtained by working in extremely dilute solution and adding various amounts of hydrochloric acid to give hydrogen ion concentrations over the range that measurements were practical, in this way the added acid acted as a buffer and prevented large changes in hydrogen ion concentration.

Since *p*H values as usually determined with the glass-electrode *p*H meter do not represent either hydrogen ion activities or concentrations, the *p*H meter was calibrated against known small concentrations of hydrochloric acid under the conditions of temperature and supporting electrolyte used in this investigation. All hydrogen ion concentrations reported were determined by reference to calibrations made in this manner.

All measurements were taken with the cell submerged in a constant temperature bath which was maintained ±0.05° at 25° and 35.8°, and ±0.1° at 17.2°.

Results and Discussion

Figure 1 shows polarograms of 5.0 millimolar chromium(III) chloride in 0.1 molar potassium chloride taken 3 minutes, 30 minutes, 60 minutes and 360 minutes after first dissolving and mixing the chromium salt. In the first curve the half-wave potential is −0.61 v. *vs.* S.C.E. In the second and third curves the first wave has a half-wave potential of −0.61 v. *vs.* S.C.E. and the half-wave potential of the second wave is −0.85 v. *vs.* S.C.E. In the final curve shown the half-wave potential is −0.85 v., which is identical with the half-wave potential of the second waves in curves two and three. When this solution was allowed to age completely it finally came to be reduced at a half-wave potential of −0.89 v. *vs.* S.C.E. This does not agree completely with the −0.91 reported by Lingane and Pecsok.[4] The 0.01% gelatin used by Lingane and Pecsok caused the reduction to become somewhat irreversible and thus a 0.02 v. more negative half-wave potential observed by them. In this investigation the authors found that the Cr(III) → Cr(II) reduction was reversible only up to about 0.005% gelatin. The pinched-down appearance of the third and fourth curves in Fig. 1 was due to a maximum, which was not completely suppressed. This maximum became suppressed completely if 0.004% gelatin was used. The fact that the half-wave potential shifts from −0.85 to −0.89 v. indicates that the intermediate forms of equation (1) are also more easily reducible than the hexaquo form, but the potential difference is so small that the rate of this second step of the transition cannot be followed by a polarographic method as described in this paper for the first step.

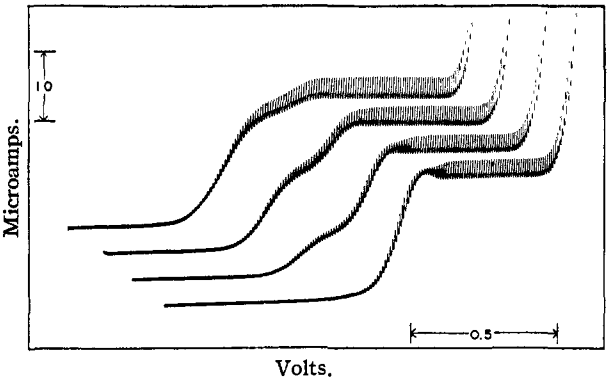


Fig. 1.—Reduction of 5 millimolar chromium(III) chloride in 0.1 molar potassium chloride containing 0.001% gelatin. Recording of waves started at 3 minutes, 30 minutes, 60 minutes and 360 minutes after first mixing solution. Each recording started at −0.045 volt *vs.* S.C.E.

The potential of −0.71 v. *vs.* S.C.E. was chosen as the potential for use in following the decrease of diffusion current of this new wave. One of the two ions shown on the left in equation (1) is reduced at the dropping mercury electrode at a potential lower than the normal complex ion found in aged solutions, but the hydrolysis equilibrium is in effect instantaneous so that the total chromium in both of these forms contributes to the reduction wave found at −0.61 volt.

The rate of transition was followed with various amounts of added acid at 25, 17.2 and 35.8°. The plots of a few of the runs made at 25° are shown in Fig. 2 with log i/i_0 plotted against time in minutes. This is essentially a plot of log $(\mathrm{Cr_t})/(\mathrm{Cr_t})_0$, where $(\mathrm{Cr_t})$ is the total concentration of the chromium in the two forms in equilibrium on the left in equation (1), since at the concentrations

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(11) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

used the diffusion currents were proportional to concentrations. The fact that these logarithmic plots are straight shows that the reaction is first order with respect to total chromium ion concentration.

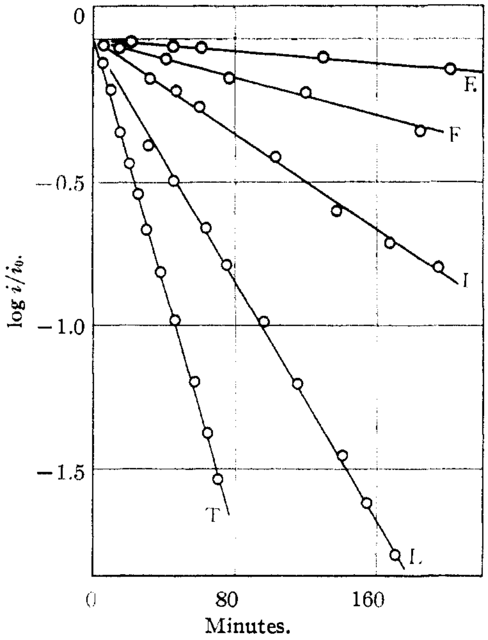

Fig. 2.—Rate data plotted according to first order relationship at pH values: E, 2.37; F, 3.00; I, 3.36; L, 3.70; T, 4.00.

From equation (1) it is seen that the $[CrCl_2(H_2O)_3OH]$ ion proceeds through the transition by exchanging one of the bound chlorides for a water molecule. The rate of this transition can be represented by

$$d(Cr_t)/dt = -k_3(Cr_2) \quad (2)$$

where (Cr_2) represents the concentration of $[CrCl_2(H_2O)_3OH]$ undergoing the first exchange of water for a chloride ion, and k_3 is the rate constant for this exchange. The equilibrium on the left in equation (1) can be represented by

$$(Cr_2)(H^+)/(Cr_1) = K \quad (3)$$

where (Cr_1) represents the concentration of $[CrCl_2(H_2O)_4]^+$ and K is the equilibrium constant.

Substituting from equation (3) into equation (2) and making the approximation that $(Cr_1) = (Cr_t)$, the expression was obtained

$$\frac{d(Cr_t)}{dt} = -\frac{k_3(Cr_t)K}{(H^+)} = -k'(Cr_t) \quad (4)$$

This approximation is justified as long as the hydrogen ion concentration is 10^{-4} or greater, which condition was maintained in this investigation.

In Table I are given the pH at which each run was made, the hydrogen ion concentration, the slope of the log i/i_0 vs. time plots, the concentration of the supporting electrolyte, and the values of k_3 calculated from treatment of the data according to equation (4).

TABLE I

RATE CONSTANTS FOR THE FIRST STEP OF GREEN TO VIOLET TRANSITION FOR CHROMIUM(III) CHLORIDE

pH	$[H^+] \times 10^4$, moles/liter	$k' \times 10^6$ per sec.	KCl, mole/liter	$k_3 \times 10^2$
		Temperature 25°		
4.00	1.42	59.9	0.4	4.5
4.00	1.42	60.3	.4	4.5
3.90	1.63	55.7	.1	4.8
3.88	1.70	55.4	.4	5.0
3.70	2.75	32.0	.1	4.6
3.50	4.47	21.4	.4	5.0
3.49	4.67	20.6	.1	5.1
3.36	6.33	12.5	.4	4.2
3.22	7.94	13.0	.1[a]	5.4
3.20	8.54	9.14	.4	4.1
3.19	8.93	11.5	.1	5.4
3.16	10.0	8.65	.4	4.6
3.10	11.2	6.45	.4	3.8
3.00	14.2	5.54	.4	4.1
3.00	14.2	5.85	.1	4.4
2.96	15.9	4.81	.1[a]	4.0
2.79	22.9	3.53	.1	4.3
2.37	63.7	1.48	.4	5.0
		Temperature 35.8°		
3.46	5.01	93.4	0.1	10.6
3.18	9.32	48.2	.1	10.2
2.80	22.9	19.4	.1	10.1
		Temperature 17.2°		
3.56	3.98	6.27	0.4	2.5
3.22	8.51	2.58	.4	2.2

[a] $NaClO_4$ used instead of KCl.

This table shows some of the runs were with 0.1 molar potassium chloride and some with 0.4 molar potassium chloride as supporting electrolyte, without any significant difference in the average rates that were found in the two cases. This indicates that the rate is probably one involving an uncharged ion, since the rate does not change appreciably with ionic strength, and also that the rate is independent of the chloride ion concentration. Further rates were determined by substituting

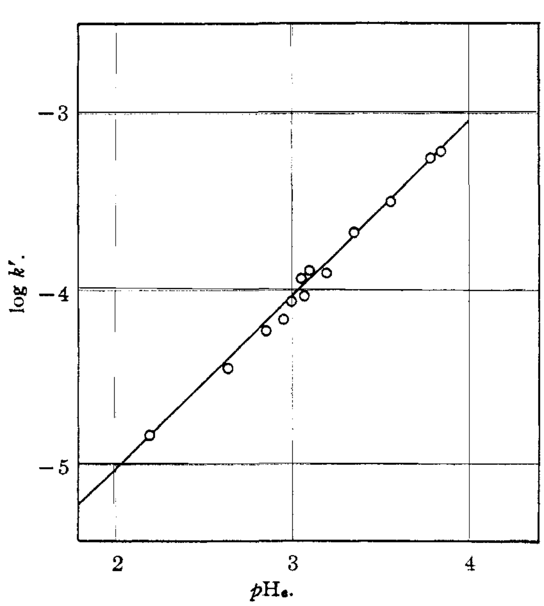

Fig. 3.—Logarithm of rate as a function of negative logarithm of hydrogen ion concentration.

sodium perchlorate for potassium chloride and again the rates obtained were identical, within experimental error. This also indicates specifically that the chloride ion concentration has no effect on the rate.

Figure 3 shows a plot of log k' against pH_c. This plot is seen to be a straight line with a slope approaching unity. This indicates that the dependence upon hydrogen ion concentration may be represented by equation (4). Many reports have been made to the effect that the presence of excess acid inhibits the transition, but this plot indicates that this inhibition comes about by repressing the hydrolysis of the dichlorotetraquochromium(III) ion.

In order to calculate k_3 for the concentrations other than 25° it was necessary to determine the hydrolysis constant of green chromium(III) chloride at the other temperatures. This was done roughly by determining the pH of fresh solutions at the temperatures in question and using the method of Lamb and Fonda[9] to calculate the equilibrium constants. The values determined were: at 17.2° $K = 1.0 \times 10^{-6}$, at 35.8° $K = 4.3 \times 10^{-6}$.

Table II gives the average values of the specific reaction rate constants determined.

TABLE II

Temperature, °C.	Constants
17.2	2.3×10^{-2}
25.0	$4.57 \times 10^{-2} \pm 0.12^{a} \times 10^{-2}$
35.8	10.3×10^{-2}

[a] Standard deviation of the mean.

A plot of the logarithm of the values of k_3 against the reciprocal of the absolute temperature was made and the points were found to fall on a straight line. From this plot the activation energy was calculated to be 13,300 calories per mole.

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SALT LAKE CITY 1, UTAH RECEIVED SEPTEMBER 5, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Oxidation of Lithium and the Alkaline Earth Metals in Liquid Ammonia

BY JOSEPH K. THOMPSON AND JACOB KLEINBERG

Solutions of the metals (lithium, calcium, strontium, and barium) were rapidly oxidized by two methods, which are designated as the "one-cell method" and the "two-cell method." The former consisted of oxidation by dropping the metal sample directly into oxygen-saturated liquid ammonia; whereas the latter method consisted of dissolving the metal in ammonia and then slowly passing this solution into a cell containing oxygen-saturated liquid ammonia so that oxidation was instantaneous. All the metals react to yield chiefly monoxide and small percentages of peroxide; no higher oxides are found in the products. All the metals yield small amounts of amide as indicated by the presence of nitrite in the oxidation products. In the case of the alkaline earth metals the products contain traces of unreacted metal as shown by the evolution of hydrogen upon addition of water. Lithium, when rapidly oxidized in liquid ammonia at −78°, forms a bright lemon-yellow solution. Measurements of the absorption spectra of oxidized solutions of lithium, sodium and potassium show that all have absorption bands reasonably close to the same wave length, 380 mμ. Since sodium and potassium are known to form superoxides upon rapid oxidation in liquid ammonia, the similarity of their absorption spectra with that of lithium supports the postulate that the latter forms a superoxide which is stable in liquid ammonia solution at −78°. Electrolysis of magnesium bromide in liquid ammonia between a magnesium anode and a platinum cathode yields blue solutions of the ionized metal. Oxidation of such solutions results in the formation of small amounts of peroxide; faint, but positive tests for nitrite are also obtained.

The literature on the oxidation of liquid ammonia solutions of lithium and the alkaline earth metals is scanty. Pierron[1] reported a 23% yield of peroxide when oxygen is bubbled through solutions of lithium in liquid ammonia. Guntz and Mentrel[2] reported the formation of gelatinous mixed oxide precipitates containing 7–9% peroxide when barium is treated similarly.

The oxidation in liquid ammonia of the alkali metals other than lithium has been thoroughly studied.[3] According to Kraus and Whyte[4] slow oxidation of potassium, and presumably of sodium also, results in the initial formation of peroxide which is reduced by excess metal to the monoxide. Ammonolysis of the latter yields amide which is subsequently oxidized to nitrite. Rapid oxidation of potassium produces chiefly the peroxide, provided the process is interrupted as soon as free metal disappears; the peroxide may then be converted to superoxide by continued oxidation. There is practically no amide formation when potassium is rapidly oxidized at −50°.[5] Schechter, Thompson and Kleinberg[6] have demonstrated that amide formation can be avoided during the rapid oxidation of sodium only under carefully controlled conditions. The purpose of the work described in this report was to study the behavior of lithium and the alkaline earth metals under the conditions which inhibited amide formation in the case of sodium.

Experimental

Method of Oxidation.—Solutions of lithium and the alkaline earth metals were oxidized by two methods, which will be designated as the "one-cell method" and the "two-cell method." The apparatus used was essentially the same as that designed and used by Schechter, Thompson and Kleinberg[6] in their studies on the oxidation of sodium in liquid ammonia. In the "one-cell method" the sample of metal was dropped into a cell containing about 75 cc. of liquid ammonia (refrigeration grade) through which dry oxygen was bubbling at a rate of about 40 cc. per minute. In the "two-cell method" the metal sample was dissolved in about

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[1] P. Pierron, *Bull. soc. chim.*, [5] **6**, 235 (1939).

[2] A. Guntz and Mentrel, *ibid.*, [3] **29**, 585 (1903).

[3] G. W. Watt, *Chem. Revs.*, **46**, 293 (1950).

[4] C. A. Kraus and E. F. Whyte, THIS JOURNAL, **48**, 1781 (1926).

[5] C. A. Kraus and E. F. Parmenter, *ibid.*, **56**, 2384 (1934).

[6] W. H. Schechter, J. K. Thompson and J. Kleinberg, *ibid.*, **71**, 1816 (1949).