

On the Standard Potential of the Cr(III)—Cr(II) Couple in 1 M NaCl Medium

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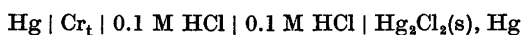
The standard potential for $\text{Cr(III)} + e^- \rightleftharpoons \text{Cr(II)}$ in the medium 1 M NaCl at 25°C has been determined; it is -429 ± 1 mV. The data are summarized in Table 1.

Experimental conditions facilitating the employment of the Cr(III)—Cr(II) couple for equilibrium analysis are described in some detail.

This communication summarizes the results of our efforts to find a convenient approach for the study of equilibria in which Cr(III) ions participate by the measurement of the potential of the Cr(III)—Cr(II) couple. The approach has been tested by the determination of the standard potential of this couple in 1 M NaCl medium.

The serious difficulties, encountered when classical methods of preparation, analysis, and emf measurements are applied, may probably be regarded as the main reason that only two systematic attempts seem to have been made to ascertain the magnitude of the Cr(III)—Cr(II) standard potential.

Benefiting from the experience gained by Mazzuchelli¹ in his exploratory work of 1905, Forbes and Richter² developed in 1917 an anaerobic technique to prepare solutions of precisely known chromium(II) chloride and chromium(III) chloride content as well as to determine the emf of the cell



where Cr_t is the chromium test solution containing 0.1 M HCl. Although due to the initially

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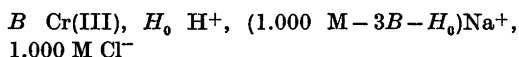
rapid decomposition of the Cr(II) ions 30–40 h were required to attain a constant emf value and a substantial correction had to be introduced for the loss of Cr(II), Forbes and Richter presented evidence² for the reversibility of the Cr(III), Cr(II)/Hg half-cell. One can calculate on the basis of their data, comprising the $[\text{Cr(II)}][\text{Cr(III)}]^{-1}$ range 0.1 to 4.7, a value of -402 ± 5 mV for the standard potential.

Forbes' and Richter's work was extended by Grube and Schlecht,³ who in 1926 studied at 18°C the Cr(III)—Cr(II) couple in chloride, sulfate, and acetate solutions. Their conclusions³ corroborate the results of the previous investigators. Two main complications arose. The log $[\text{H}^+]$ range available for the measurements is narrow; at high acidities the chromium(II) ions become rapidly oxidized by H^+ while at low hydrogen ion concentrations the sluggish hydrolysis of Cr(III) must be taken into account. Moreover, the complex formation equilibria of the chromium(III) ions are attained at room temperature so slowly that emf measurements of long duration are required which can be interpreted only if the concurrent oxidation of Cr(II) is prevented throughout.

METHOD OF INVESTIGATION

The experimental approach which has proved to be practical for the $\text{Eu}^{3+} - \text{Eu}^{2+}$ couple^{4,5} has been mainly followed.

We started each series of experiments with a solution of the general composition

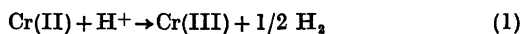


which will be denoted in the following discussion by S_0 , while the solution arising from S_0 by electrolytic reduction will be represented by S .

The B range 5 to 28 mM has been investigated. In more dilute solutions difficulties were encountered. When, *e.g.*, in a 1 mM test solution the surface of the mercury redox electrode was renewed (see later), the redox potential was found to increase at a diminishing rate for about an hour and then became practically constant. Its starting value was in accord with the data obtained in the higher B range but the steady state value indicated that, because of the accumulation of impurities, the ratio $[\text{Cr(II)}][\text{Cr(III)}]^{-1}$ was considerably lower in the vicinity of the electrode than in the bulk solution.

With the available current supply the study of more concentrated solutions would require an unpractically long experiment.

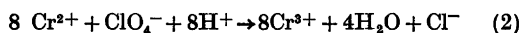
In each case, the starting value for the proton excess, H_0 , was chosen to equal B . As we have not been able to suppress entirely the reaction



the hydrogen ion concentration of the test solution, h , diminished slowly in the course of a series of measurements. As glass electrode data indicated, in no case did the value of h drop below 0.1 mM, however. Coulometric alkalification experiments afforded evidence that under the present conditions the hydrolysis of Cr(III) is negligible for $\log h > -4$.

In order to minimize the variation of the activity factors of the reacting species, all the test solutions were made to contain 1 M Cl^- by the addition of NaCl. The standard state has been defined so that the activity factors of the reacting species tend to unity as the composition of the solution tends to 1 M NaCl.

Our attempts to study the $\text{Cr}^{3+} - \text{Cr}^{2+}$ couple in perchlorate media, which was our original intention, have failed. As soon as an appreciable amount of Cr^{2+} had been generated, the reaction

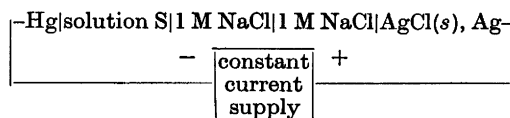


started to proceed and within a short time the hydrogen ion concentration decreased so

much in the vicinity of the cathode that some chromium(III) hydroxide precipitated.

We have not been able to prepare chloride-free chromium(II) perchlorate solutions by chemical methods either; reduction with the amalgams of zinc and of cadmium, and dissolution of chromium metal of spectrographic purity in perchloric acid were tried.

The *electrolytic generation* of Cr(II) ions was carried out in the circuit



The current supply was synchronized with a digital counter and throughout the electrolysis the current strength was recorded each minute. The number of moles of electrons introduced into S at cathodic reduction, μ , is believed to possess an uncertainty of less than 0.01 %.

Following an electrolysis step a certain period of time was found to be required for the attainment of a steady state.

An excess of Cr(II) ions is built up in the vicinity of the cathode during the electrolysis; its decline was followed by measuring the emf between the cathode pool and one of the other two mercury electrodes placed in the diametrically opposed receptacles of the measuring vessel. Generally about 15 min were needed to reach a uniform concentration throughout the test solution. At this stage each of the mercury electrodes should exhibit the same value for the redox potential and any further variation should be explainable on the basis of reaction (1). This condition entails the validity of the equation

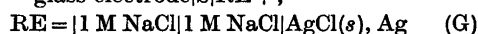
$$[\text{Cr(II)}] = \mu/V - (H_0 - h) \quad (3)$$

where V represents the volume of the test solution and μ the moles of electrons introduced at cathodic reduction. An additional complication has arisen at the highest B levels studied and in the experiments where part of the Cr(II) ions were reoxidized electrolytically. In these cases the redox potential of the test solution was found to change monotonically for a period covering in some instances as much as 12 h, while the hydrogen ion concentration varied only slightly. As the trend in the redox

potential had opposite signs in the reduction and in the oxidation experiments, we ascribe the drift to the slow attainment of the chloride complex formation equilibria which become displaced by electrolysis.

All the data considered for the evaluation of the standard redox potential correspond to the steady state and satisfy eqn (3).

The instantaneous value of the hydrogen ion concentration, h , in the chromium test solutions was measured by determining the emf of the cell —glass electrode|S|RE +;

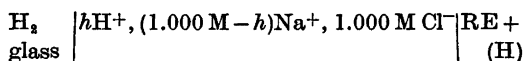


The emf of this cell at 25 °C may be expressed by

$$E_{\text{G}} = e_{\text{RE}} - e_{\text{G},0} - 59.16 \log h + e_j \quad (4)$$

In eqn. (4) e_{RE} represents the potential of the reference half-cell RE, e_j is the symbol for the liquid junction potential arising between S and 1 M NaCl and $e_{\text{G},0}$ denotes a term remaining constant in a series of measurements but, due to the uncontrollable changes slowly occurring in the surface layer of the glass electrode, its magnitude has to be determined in each experiment.

For the estimation of the liquid junction potential, e_j , the emf of the cell



was determined as a function of h in the range 0.01 to 0.06 M. The data can be described to within 0.1 mV by the simple equation

$$e_j = (66 \pm 1)h$$

Incidentally these measurements indicated that under the present experimental conditions the glass electrode may be regarded to be equivalent with the hydrogen half-cell to within a few hundredths of a mV.

Assuming a concentration distribution of the Henderson type, this liquid junction potential can be estimated with the conductance values of 1 M HCl and 1 M NaCl solutions as well as with the relevant transport numbers, all taken from Ref. 6, to $e_j = 59.16 \log (1 + 2.87_5 h)$. For the low h values in question this equation may be simplified to $e_j = 74h$. The deviation from the data may be explained by our approximation that the conductance of HCl—NaCl

mixtures of 1 M Cl^- is a linear function of the conductances of 1 M HCl and 1 M NaCl solutions.

The potential of the reference half-cell, e_{RE} , was evaluated at regular intervals by measuring the emf of cell (H) with a solution containing 10.00 mM H^+ . In accordance with our choice of standard state the potential of the hydrogen half-cell is given by $59.16 \log h p_{\text{H}_2}^{-1/2}$.

During the six months when the final measurements were carried out, e_{RE} proved to change by but 0.2 mV, from 235.4 to 235.2 mV, thus no appreciable contamination occurred in RE.

A check on this e_{RE} value may be obtained by recalling that on the scale of the conventional activity factors — reference state 1 M ideal solution in the solvent water — our e_{RE} value equals $e^0(\text{AgCl}, \text{Ag}) - 118.32 \log \gamma_{\text{HCl}}^{\text{trace}}$, where $e^0(\text{AgCl}, \text{Ag}) = 222.3_6 \pm 0.1$ mV⁷ denotes the standard potential of the Cl^- , AgCl/Ag half-cell, and $\gamma_{\text{HCl}}^{\text{trace}}$ is the symbol for the trace activity factor of hydrochloric acid in 1 M NaCl. Neglecting the difference between volume and weight molarities we may take Harned's value⁸ for $\log \gamma_{\text{HCl}}^{\text{trace}}$ (1 m NaCl) = -0.12_4 , thus e_{RE} can be estimated to be 237.0 mV. The deviation, about 2 mV, may be ascribed to the lattice imperfections in our silver electrodes which were prepared by electrolysis. Another reason might be the difference in the bromide contamination levels.

To obtain the actual value of $e_{\text{G},0}$ the emf of cell (G) was measured in each experiment prior to the generation of Cr(II) ions, thus with $h = H_0$.

The redox potential of the Cr(III)—Cr(II) couple was determined by measuring the emf of the cell



Provided that the chloride complex formation equilibria had been reestablished in S after an electrolysis step, the emf of cell (R) may be expressed by the equation

$$E_{\text{R}} = e_{\text{RE}} - e_{\text{R},0} - 59.16 \log \frac{[\text{Cr(III)}]}{[\text{Cr(II)}]} + e_j \quad (5)$$

where $e_{\text{R},0}$ represents the standard potential whose magnitude is sought. As the total chromium concentration was always less than 3 % of the total molarity, the ratio $[\text{Cr(III)}] \times$

$[\text{Cr(II)}]^{-1}$ differs from $[\text{Cr}^{3+}][\text{Cr}^{2+}]^{-1}$ by the constant factor $(1 + \sum \beta_n')(1 + \sum \beta_n)^{-1}$ where β_n and β_n' denote the formation constants of the n chloride bearing chromium(III) and chromium(II) complex species.

According to eqns. (3) and (5) each pair of simultaneous E_R , E_G data obtained in the steady state, when only reaction (1) proceeds, furnishes a value for $e_{R,0}$

$$e_{R,0} = e_{RE} - E_T + e_j - 59.16 \log [(B - \mu/V + H_0 - h)/(\mu/V - H_0 + h)] \quad (6)$$

EXPERIMENTAL

Materials and analysis

Chromium(III) chloride stock solutions were prepared by dissolving chromium pellets, free from spectrographically detectable impurities (supplied by Johnson, Matthey & Co., London), in a small excess of freshly distilled azeotropic hydrochloric acid. At the initial stage some hydrogen sulfide was found to evolve. Probably all the sulfur impurity could be flushed out, however, as H_2S by the vigorous stream of hydrogen generated throughout the dissolution.

The chromium content of the stock solutions, always kept at around 0.1 M, was determined iodometrically after having transformed Cr(III) to Cr(VI) with a hot alkaline hydrogen peroxide solution. The proton excess of the stock, also made to have a value of around 0.1 M, was determined potentiometrically with a glass electrode by coulometric alkalification.

Dust and basic impurities (mainly carbonate ions) were removed from commercial *sodium chloride* batches of *p. a.* quality by preparing first a saturated solution, filtering it through sintered glass and then precipitating at 0°C by hydrogen chloride finely divided NaCl crystals. The crystals were dried and finally ignited at 360°C . In an effort to keep bacterial and other contamination at a minimum, the test solutions were prepared *in situ* by introducing into the cell vessel first the chromium stock, then a weighed amount of NaCl and finally the required volume of water. The volume of the test solution was chosen to have a value between 75.0 and 100.0 ml.

Nitrogen was taken from a cylinder and freed from oxygen by passing it in succession through a column of activated copper kept at 170°C , distilled water, 1 M NaCl, and two solutions containing 0.1 M CrCl_2 and 0.8 M NaCl maintained in intimate contact with amalgamated zinc grains. In the last stage of purification the gas stream was lead through sintered glass of porosity G4 to remove floating dust.

To check the purity of this nitrogen, the gas was in the course of a series of emf meas-

urements allowed to build up a small overpressure over the test solution and then the gas stream was stopped. After a period of several hours, while the electrolysis and the emf measurements were continued, the nitrogen flow was reestablished at atmospheric pressure. In no case, even with solutions containing 0.1 mM Cr(II), was the extinguishment or the reintroduction of nitrogen found to cause an appreciable change in the emf value.

Mercury was purified, as usual in this laboratory, by double distillation at a partial pressure of oxygen just insufficient to give rise to the formation of HgO . Dust and other impurities gathering on the surface during preservation were eliminated by filtration through sintered glass immediately before use.

To estimate the trace amount of *oxidizing agents* left in our test solutions, coulometric redox titrations were made with a low current strength, *e.g.* 0.5 mA. It was then observed that while the current was passed for several minutes, E_R remained constant at the starting value of around -20 to -30 mV and then a dramatic increase in E_R ensued. The assumption that the moles of electrons needed to be introduced at cathodic reduction to achieve a monotonic increase in E_R equals the equivalents of oxidizing impurities present, yields a contamination level of $20 \mu\text{M}$. As the emf of the cell $-\text{Ag, AgCl(s)} | 1 \text{ M NaCl} | \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg} +$ has the value of 45.4 mV^* and this is not far from the $-E_R$ value found with the Cr(II)-free starting solutions, the contaminant consists probably of calomel not removable from the mercury through simple filtration. For the high B values studied in the present work this amount of impurities may be regarded as negligible.

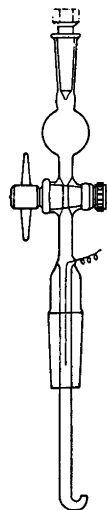


Fig. 1a. Mercury electrode for measurement of the redox potential. The stopcock is made from self-lubricating teflon.

Electrodes and apparatus

In each experiment three *mercury electrodes* were employed. The first, forming a pool in the central receptacle of the vessel, served as the cathode, while the other two were inserted to measure the redox potential of the test solution. One of them was similar to the cathode while the second is illustrated in Fig. 1a. This electrode was designed to make possible the convenient renewal of the mercury surface, the overflow gathered in a receptacle. To avoid contamination with grease a teflon stopcock was built into the electrode vessel.

In the initial stage of every series of measurements all the three electrodes yielded coincident redox potential values, indicating the establishment of a steady state in the test solution. As the experiment proceeded, the electrodes having a stationary surface, the cathode, and the stationary pool, gave emf values increasingly lower than the emf value measured with a fresh mercury surface. At the end of some experiments of several days duration a difference as great as 5 mV was found. Obviously the surface of the stationary electrodes became slowly covered by substances, such as particles originating from filter paper and other dust, catalyzing the oxidation of Cr(II) by H^+ . As a consequence in the layers adjacent to the stationary electrode surfaces the ratio $[Cr(II)][Cr(III)]^{-1}$ was smaller than in the bulk.

The emf values measured with the stationary electrodes were ignored as unreliable and for all the $e_{R,0}$ calculations the emf value obtained with a fresh surface was accepted, provided it was found reproducible to within 0.1 mV. In each experiment this degree of reproducibility could be easily attained as soon as the chloride complex formation equilibria had been reestablished after an electrolysis step; the data of Fig. 1b show some typical results.

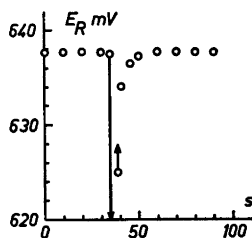


Fig. 1b. Effect of the renewal of mercury surface on the redox potential; E_R as a function of time. The electrode was flushed in the 35th second. The test solution contained 0.72 mM Cr(II), 1.24 mM Cr(III), and 1.75 mM H^+ . The E_R versus time data were obtained automatically by programming a digital voltmeter to take a reading each second, for clarity only a few points selected at random are shown.

Glass electrodes of Thalamid type supplied by Schott & Gen., Mainz, were used throughout this work. In the acidity range of interest they have often been compared and found to be equivalent to within 0.1 mV with the hydrogen half-cell.

Platinum nets of 2×2 cm size coated cathodically by a thick layer of silver crystals served as electrodes in the coulometric circuit. For each series of emf measurements two Ag,AgCl electrodes, also prepared by electrolysis and covered by a thin AgCl layer, were employed, the emf between them was never found to exceed 0.1 mV.

The cell arrangement and other experimental equipment were similar to that described in a preceding communication of this laboratory.⁵

The experiments were carried out automatically with the programmable data acquisition system constructed for precision potentiometry by Dr. Tom Wallin and one of the present authors. The E_R and E_G data possess a precision of 0.1 mV, the number of ampere-seconds passed through the test solution were measured with an uncertainty not exceeding 0.01 %.

Current levels between 0.5 and 5 mA were chosen, depending on the chromium concentration. Following an electrolysis step, both E_R and E_G were measured at 1 min intervals for at least an hour after the establishment of the steady state. Moreover, in every series of experiments two or three measurement intervals of 12 h duration were inserted. A complete set of measurements took a minimum of three days. The significance of these details is discussed in the Results section.

RESULTS

The standard potential values deduced from the final series of measurements, in which a number of precautions were taken to attain a high precision, are summarized in Table 1. This covers the chromium concentration (and consequently also the approximate hydrogen ion concentration) levels 5, 10, 22, and 27 mM; at each level the ratio $[Cr(III)][Cr(II)]^{-1}$ is seen to have been made to vary considerably, the extreme values being 7 and 0.2.

The data presented in Table 1 appear to afford evidence for the validity of our basic assumptions expressed by eqns. (3) and (5) as the $e_{R,0}$ values do not show appreciable systematic trend with any of the main experimental variables: the total chromium concentration, the ratio $[Cr(III)][Cr(II)]^{-1}$, and the acidity.

To put this conclusion, which represents the

Table 1. Survey of results.

h mM	[Cr(II)] mM	[Cr(III)] mM	$-e_{R,0}$ mV	h mM	[Cr(II)] mM	[Cr(III)] mM	$-e_{R,0}$ mV
28.05	8.81	17.9	428.8	10.64	5.55	4.53	428.1
27.72	9.63	17.1	429.7	10.60	6.30	3.78	428.2
27.60	11.8	14.9	429.7	10.56	7.10	2.99	428.5
27.60	13.2	13.5	429.9	10.28	7.65	2.43	430.5
27.07	16.1	10.6	430.2*	10.32	8.12	1.97	429.6
27.07	13.8	12.9	428.9*	10.16	8.38	1.70	431.0
24.11	2.99	19.3	429.4	9.85	8.18	1.90	428.8*
23.92	2.80	19.4	430.6	9.25	7.80	2.28	429.8*
23.46	4.52	17.7	430.2	10.73	2.69	7.39	431.5
23.38	4.45	17.8	429.6	10.73	3.50	6.58	430.7
22.48	5.74	16.5	431.3	10.16	5.36	4.72	429.5
22.13	7.59	14.7	431.0	10.16	6.16	3.92	428.6
21.87	9.52	12.7	430.5	10.00	6.81	3.27	429.1
21.62	11.5	10.8	431.1	4.96	1.43	3.33	430.0
21.29	13.3	8.90	431.7	4.54	1.83	2.93	429.0
10.89	1.81	8.27	427.9	4.04	2.14	2.62	428.8
10.84	2.24	7.84	427.9	3.62	2.54	2.23	429.0
10.76	2.64	7.44	428.5	3.13	2.87	1.90	428.4
10.76	3.13	6.96	428.4	2.89	3.00	1.76	427.6
10.64	3.80	6.28	428.8	2.71	3.07	1.70	427.8
10.64	4.28	5.80	429.0	1.97	3.25	1.51	428.3
10.64	4.76	5.32	428.1				

chief result of this work, into quantitative terms we may compare the grand average of all the 43 points $e_{R,0} = -429.4$ mV with particular averages. The set of data corresponding to the four chromium concentration levels studied yield the $-e_{R,0}$ values: 429.5 mV (27 mM), 430.6 mV (22 mM), 429.1 mV (10 mM) and 428.6 mV (5 mM). The 23 data found with solutions of $[\text{Cr(III)}][\text{Cr(II)}]^{-1} > 1$ furnish the average $e_{R,0} = -429.5$ mV, while the 20 points with $[\text{Cr(III)}][\text{Cr(II)}]^{-1} < 1$ $e_{R,0} = -429.2$ mV. We would therefore propose as the most probable value

$$e_{R,0} = -429.5 \pm 1 \text{ mV}$$

The experiments in which chromium(III) ions were anodically generated in a prerduced solution provide additional support for this estimate. These oxidation experiments, marked with an asterisk in Table 1, are seen to yield $e_{R,0}$ values agreeing closely with the others. Thus we may have little doubt that the potential measured with a fresh mercury surface may be regarded as reversible.

Our value for the standard potential has thus been found to be about 30 mV more negative than the estimates which can be

derived on the basis of the work of the previous investigators^{2,3} who studied dilute chromium solutions containing some hydrochloric acid. As the formation constants of the chromium(III) chloride complex species are not yet ascertained, the medium effect on the standard potential cannot be exactly calculated.

The following arguments suggest, however, that our result is in accordance with the conclusion of the classical investigators. Ignoring the activity factor variations and neglecting complex formation in the dilute solutions of Forbes² and of Grube³, the assumption $[\text{Cr(II)}] = [\text{Cr}^{2+}]$ leads to the relationship -429.5 (standard potential in 1 M NaCl medium) = -400 (standard potential in dilute chromium chloride solution) $-59.16 \log(1 + \sum \beta_n)$ where β_n denotes the formation constant of $\text{CrCl}_n^{(3-n)+}$. Hence we obtain for $\log(1 + \sum \beta_n)$ a value of around 0.5. This conjecture falls within the limits of the widely different estimates¹⁰ reported for the β_n 's.

Finally we have to discuss the time requirement for the performance of a complete series of emf measurements.

The E_R data of Table 1 represent the steady state in which exclusively reaction (1) was

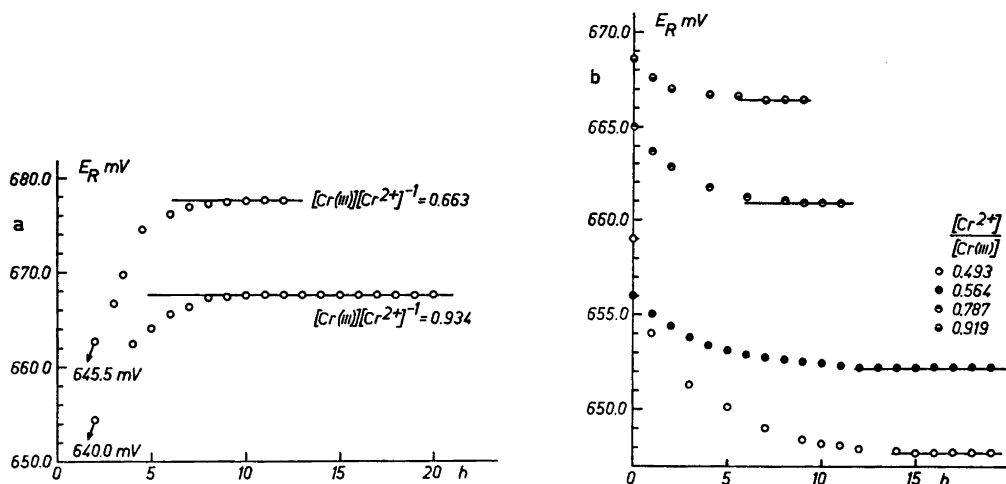


Fig. 2. Illustration of slow equilibration ensuing (a) the generation of Cr(III) ions and (b) the generation of Cr(II) ions; E_R as a function of the time elapsed after the termination of the electrolysis. In each experiment the total chromium concentration was kept at 26.69 mM. The horizontal lines represent the emf values corresponding to the attainment of the complex formation and dissociation equilibria. The emf values below the arrows in Fig. 2a were taken a few seconds after the completion of the oxidation.

found to occur. After each step of electrolysis both E_R and E_G were recorded at least for an hour. Moreover, to test whether the chloride complex formation equilibria were really attained, the reduction was often interrupted for 12 to 20 h but the $e_{R,0}$ value always proved to remain constant to within 0.2–0.3 mV. Such long interruptions have a detrimental effect on the precision of the standard potential evaluation since it now involves the unavoidable drift of the glass electrode. A considerable part of the spread in the $e_{R,0}$ values of Table 1 may be ascribed to this source of uncertainty.

Periods exceeding one hour were needed for the attainment of the steady state only in the oxidation experiments and in the reduction steps at the 27 and 22 mM chromium levels with points corresponding to a low $[Cr(II)] \times [Cr(III)]^{-1}$ value. As the generation of Cr(II) proceeded, and the ratio $[Cr(II)][Cr(III)]^{-1}$ approached unity even at these high concentrations the steady state was found to be reached within an hour.

The sluggish equilibration ensuing Cr(III) generation is illustrated in Fig. 2a, while the time dependence of E_R in some typical reduction experiments is shown in Fig. 2b. No appreciable

variation in E_G could be detected in the course of these measurements.

We may then conclude that for equilibrium analysis it is practical to build up a $[Cr(II)] \times [Cr(III)]^{-1}$ ratio of around unity before introducing the ligand.

When this and the other precautions described earlier in this work are strictly kept, our experience indicates that for experiments of a duration not exceeding about 12 h the parasitic reaction $Cr^{2+} + H^+ \rightarrow Cr^{3+} + \frac{1}{2}H_2$, may be neglected. Thus complex formation equilibria between Cr(III) and some weak acids might also become accessible to an experimental study with the Cr(III)—Cr(II) couple.

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