An Investigation of the System Cr(III)/Cr(II) by Digital Polarography, at Dirrerent Cr(III) Concentrations, at Varying pH, and in Different Supporting Electrolytes.

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ABSTRACT

One of the implications of Marcus theory of electron transfer is that α, the electrochemical transfer coefficient, would not be constant, but would be a function of potential. Recent work has tended to confirm this implication.

To examine this possible potential-dependence of α, the system Cr(III)/Cr(II) was investigated by digital polarography, at different Cr(III) concentrations, at varying pH, and in different supporting electrolytes. Most of the resulting rate data do suggest a potential-dependence of α.

Apparent heats of activation were obtained for three of the supporting electrolytes investigated, and from these a calculation was made of the magnitude of the potential-dependence predicted by Marcus theory. There was little correlation between the magnitude of the potential-dependence predicted by Marcus theory, and that actually found.

INTRODUCTION

For an electrochemical redox reaction, one may distinguish five states for a soluble oxidized species O and reduced species R.

I. O in bulk of solution outside diffuse double layer and n electrons e in the electrode.

II. O in outer plane of closest approach and n electrons e in electrode.

$\neq$ Transition state.

III. R in outer plane of closest approach.

IV. R in bulk of solution outside diffuse double layer.

Delahay,[1] following Parson's formulation, defines the electrochemical transfer coefficient α in terms of the potential-dependent part of the standard free energy difference $F^{o}_{III}-F^{o}_{II}$. In this way, the calculation of $F^{o}_{\neq}$, needed for the rate constant, can be formulated without a detailed model of the transition state, by assuming the potential-dependent part of the free energy difference between states $\neq$ and II may be expressed as a constant fraction α of the potential-dependent part of the free energy difference between states II and III. Thus,

$$(F^{o}_{\neq})_e - (F^{o}_{II})_e = \alpha \left[(F^{o}_{III})_e - (F^{o}_{II})_e\right]$$

where the subscript e denotes the potential depen-

dent part. Van Rysselberghe,[2] however, considers α must be defined in terms of $F^{o}_{III} - F^{o}_{II}$ and not in terms of the potential-dependent part of this difference. These formulations lead to the prediction, in absence of double-layer effects, that α would be independent of potential. That is,

if $\Delta F^{*} = F^{o}_{\neq} - F^{o}_{I}$

$$k_{f,h} = k^{o}_{f,h} \exp\left\{\frac{-\alpha n \mathcal{F}}{RT} E\right\}$$

$$\ln k_{f,h} = \frac{-\alpha n \mathcal{F}}{RT} E + \ln k^{o}_{f,h}$$

$$\frac{\partial \ln k_{f,h}}{\partial E} = -\frac{\alpha n \mathcal{F}}{RT}$$

Here the subscripts f,h indicate the forward (f) rate constant of a heterogeneous (h) reaction. R, T, and $\mathcal{F}$ have their usual significance.

However, Marcus[3-8] has formulated a theory of electron transfer which attempts to construct exactly what is avoided in the above, i.e., a detailed model of the transition state. This model assumes only a weak electronic interaction between, in the electrochemical case, the electrode and reactant. Marcus also considers that an electron transfer reaction may proceed by way of intermediate states whose electrical polarization is not in equilibrium with the

field arising from the charges present. This model may be considered to be an application of the Frank-Condon principle. His final equations are thus derived for non-equilibrium conditions:

$$\Delta F^* = w^r + m^2 Y$$

$$m = -\left(\tfrac{1}{2} + \frac{n\mathcal{F}\eta + w^p - w^r}{2Y}\right)$$

$$\Delta F^* = w^r + \left(\frac{Y}{4} + \frac{n\mathcal{F}\eta + w^p - w^r}{2} + \frac{(n\mathcal{F}\eta + w^p - w^r)^2}{4Y}\right)$$

$$\frac{Y}{4} + \frac{n\mathcal{F}\eta}{2} \quad \frac{w^p + w^r}{2} \quad \frac{(n\mathcal{F}\eta + w^p - w^r)^2}{4Y}$$

η = overvoltage = $E - E_o'$, where E_o' is the standard potential. (Note this is different from the electrochemical overvoltage, $\eta = E - E_{rev}$ where E_{rev} is the equilibrium potential.)

w^r = work needed to bring reactant and electrode together.

w^p = comparable quantity for products.

Y = energy required to reorganize the coordination shell during activation = $Y_i + Y_o$. See Reference 9.

These equations may be applied for a "nonadiabatic reaction", i.e., a reaction where the probability of passage along the potential energy surface characteristic of reactants to the potential energy surface characteristic of the products is small.

One may assume $w^p = 0 = w^r$, if double-layer effects are neglected (or if the data have been previously corrected for double-layer effects); then

$$\Delta F^* = \frac{Y}{4} + \frac{n\mathcal{F}\eta}{2} + \frac{(n\mathcal{F}\eta)^2}{4Y}$$

Then $$k_{f,h} = k_{f,h}^{\circ} \exp\left(\frac{-\Delta F^*}{RT}\right)$$

$$\ln k_{f,h} = \frac{-\Delta F^*}{RT} + C$$

$$= \frac{-1}{RT}\left(\frac{Y}{4} + \frac{n\mathcal{F}\eta}{2} + \frac{(n\mathcal{F}\eta)^2}{4Y}\right) + C$$

$$\frac{\partial \ln k_{f,h}}{\partial \eta} = \frac{-n\mathcal{F}}{RT}\left(\frac{1}{2} + \frac{\eta}{2Y}\right)$$

For $n = 1$,

$$\alpha = \frac{-\partial \ln k_{f,h}}{\partial \eta}\left(\frac{RT}{\mathcal{F}}\right) = \left(\frac{1}{2} + \frac{\eta}{2Y}\right)$$

Thus Marcus theory would predict a potential dependence of α. This particular set of equations applies to a heterogeneous reaction of the type Marcus classifies as Class III,[10] i.e., redox reactions in which the coordination shell of the oxidized form has quite different interatomic distances compared to the reduced form.

One example of this type of reaction is the one studied in this research,

$$Cr(H_2O)_6^{3+} + ne^- \longrightarrow Cr(H_2O)_6^{2+}.$$

This is presumed to be an outer-sphere reaction,[11] and so fulfills Marcus' condition of weak interaction between the reactant and electrode. Also, the relatively low rate constant[12] (1.0×10^{-5} cm/sec at

20°C in 1 M KCl) fulfills the condition of non-adiabaticity.

Koutecky's[13,14] analysis of irreversible electrode processes of the type

$$O + ne^- = R$$

relates the ratio i/i_d to Λ, where

i = current

i_d = diffusion current

$$\Lambda = (12/7)^{\frac{1}{2}} \frac{k_{f,h}\, t^{\frac{1}{2}}}{D_O^{\frac{1}{2}}}$$

D_O = diffusion constant of oxidized species O.

t = drop time in sec.

The relation between Λ and i/i_d has been tabulated, and reproduced by Delahay.[15] Thus, it is obvious that if i/i_d is known, Λ may be found, and because

$$\ln \Lambda = \ln k_{f,h} + C$$

the slope of a plot of $\ln \Lambda$ versus potential should yield α, for an irreversible process.

Parsons and Passeron[16] published some data for the Cr^{+3}/Cr^{+2} reaction, indicating that a potential dependence was observed for the transfer coefficient. This work is a continuation of their investigation. To clearly establish the potential-dependence of α

would be evidence favoring the Marcus theory of electron transfer, and evidence against the older formulation typified by Parson's presentation.

EXPERIMENTAL

Normal procedure was to obtain a current-voltage curve using D.C. digital polarography. Philbrick P65 and P65AU amplifiers were used as a current measurer and follower, respectively. All data were corrected for background current by graphical subtraction, and the i/i_d ratios were corrected for mass transfer using Koutecky's analysis.[17] Points on the polarograms were usually recorded at 10 mV. intervals.

Drop times were kept approximately constant, and were obtained from chart speed and peak spacing. If the variation was greater than $\pm$ 0.03 sec., the values were corrected to 4.15 sec. Unless otherwise noted, the temperature was 25.0° $\pm$ 0.2°. The cell design is shown in Figure 1.

A gas train was constructed using chromous and vanadous traps; high purity (Matheson, silver tank) nitrogen was used for deaeration. Nitrogen was also passed over the surface of the solution during a run. Except where otherwise specified, all runs were made at pH of 2.0 $\pm$ 0.1.

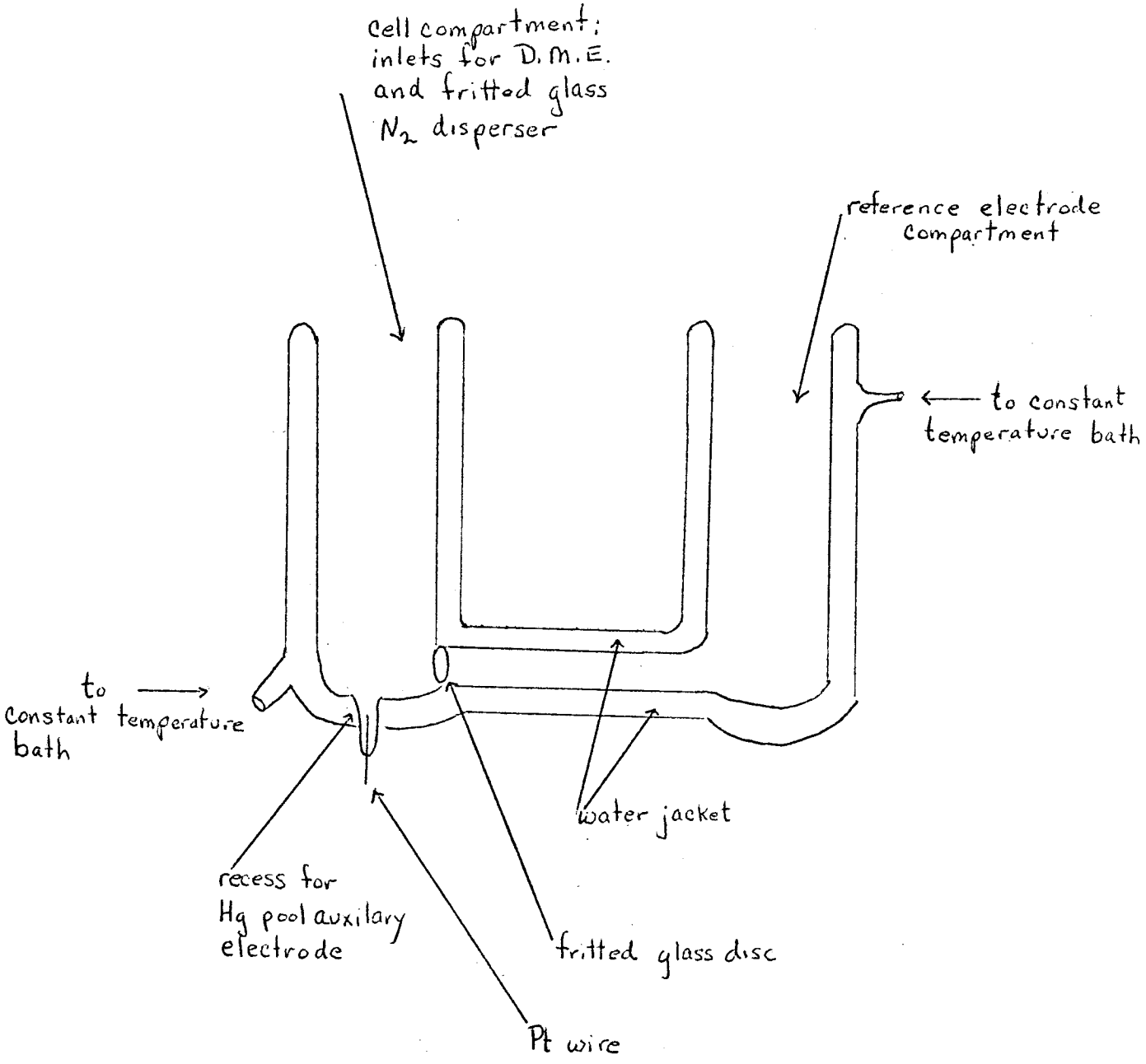

Figure 1. Schematic of cell design. A commercial electrode (Sargent SCE) was used as the cell reference electrode, with NaCl crystals and solution rather than KCl.

A modified saturated calomel electrode was used, with NaCl rather than KCl, to avoid precipitation at the liquid-electrode junction of $KClO_4$ in the perchlorate solutions. This cell reference electrode was checked against a massive SCE electrode, constructed according to the method described in Ives[18]. Over a period of a few months, the potential of the cell reference electrode was found to be constant to ± 1 mV.

Purified charcoal was prepared by leaching activated charcoal (Matheson, Coleman and Bell, CX 655) with concentrated HCl under an N_2 atmosphere in a Soxhlet extractor until the extract was clear, then extracting with water until the extract was the same pH as the distillate. The purified charcoal was kept in the extractor under N_2 until ready for use. Some solutions were treated with this purified charcoal, but no systematic variations were observed in the polarographic behavior of the treated solutions compared to the untreated solutions.

Preparation of Cr(III) Solution:

A solution of 0.1 F $Cr(H_2O)_6^{3}$ was prepared by reduction of CrO_3 (Baker and Adamson, reagent grade) with a 10% solution of H_2O_2. The resulting dark blue solution was boiled to remove traces of H_2O_2, and

made 1 F in $HClO_4$. All solutions were made with triply-distilled water. A u.v.-visible spectra was taken. According to the criterion established by Altman and King,[19] the size and appearance of the peak at 230 mμ indicated a very small degree of polymerization. The ratio of absorbance at 230 mμ and 260 mμ was: $\frac{A_{230}}{A_{260}} = 0.26$.

Preparation of $NaClO_4$:

$NaClO_4$ was prepared by combining approximately equimolar concentrations of NaOH and $HClO_4$. The pH was then adjusted to 2.0.

Preparation of KI Solutions:

The KCl and KBr solutions were made directly from the salts (Matheson, reagent grade) and were adjusted to pH of 2.0 before a run. This procedure was not suitable for the KI solutions, because of air oxidation of the acidic solution. Therefore, the KI solutions were acidified after deaeration, and the uncertainty of the pH in these solutions was $\pm$ 0.2 pH units.

Preparation of $Al(ClO_4)_3$ Solutions:

A mother solution of $Al(ClO_4)_3$ was prepared by attack at room-temperature (to avoid reduction of

ClO_4^- to Cl^-) of 54 g. of Al in one liter of 3M $HClO_4$. Attack was initiated by a globule of mercury. In a few hours, most of the Al had dissolved, with some remaining to prevent mercury attack. An attempt was made to determine Al gravimetrically as the oxide, and gave unsatisfactory results. A determination was then done by precipitating the Al with 8-hydroxyquinoline, and yielded satisfactory precision. However, it was noticed that the pH, initially adjusted to 2.0 before a run, increased during the course of the run, and would stabilize after a period of a few hours to 3.4. Consultation with the literature[20,21] indicated that a slow equilibrium was involved in the hydrolysis of $Al(ClO_4)_3$ solutions, with the hydrolyzed species uncertain, but believed to be $[Al_2(OH)_2]^{4+}$ and $[Al_{13}(OH)_{32}]^{7+}$. The data gathered with this solution were also obviously spurious; the currents would change with time, and more dilute concentrations of the electrolyte gave slower rates, before double-layer corrections, than more concentrated ones, for the same Cr(III) concentrations at the same potentials.

An attempt was made to salvage this solution by titrating with $HClO_4$ to a pH of 2.0, and adding

titrant as the pH changed, until a pH of 2.0 was maintained for 16 hours. However, satisfactory results were still not obtained, so this solution was discarded, and a new one prepared.

The second Al solution was prepared in the same manner as the first, except that 54 g. of Al were used in one liter of solution 6 M in $HClO_4$. The Al was again analyzed as the oxine. The solution prepared in this manner maintained a constant pH, and gave reasonable results.

pH Study of Cr(III) in 0.5 F $NaClO_4$:

A series of solutions was prepared, with the pH ranging from 2.0 to 4.0. Care was taken to avoid exposing the Cr(III) solution to a pH greater than 4.0, to avoid problems with polymerization, etc. A Leeds & Northrup pH meter was used to determine the pH, with a modified saturated calomel electrode (NaCl instead of KCl).

Heat of Activation Studies:

A constant temperature bath, equipped with stirrer and heater, was used to control the bath temperature to $\pm 0.05^{\circ}$. A centrifugal pump circulated the bath water through the water jacket of the cell. The temperature variation within the cell

itself did not exceed $\pm 0.3^{\circ}$ for a given run, in those cases where heat losses were greatest.

RESULTS

The first variable studied in the Cr(III) system was the Cr(III) concentration, at constant electrolyte strength (0.5 F $NaClO_4$). There, of course, should be no effect on the rate constant for variations in the chromium concentration. Over a range of dilute Cr(III) concentrations, (0.3 mM - 1.0 mM), this proved to be the case. For concentrations greater than 1 mM (2 mM, 3 mM, 3.5 mM, 4.0 mM) the data were increasingly erratic. At 2 mM concentrations there occasionally would be polarograms demonstrating maxima behavior; less frequently, there would be distortion of the peak shape. For concentrations of 3.0 mM and greater, the maxima behavior would be more frequent and more pronounced. Even those polarograms at 2 mM Cr(III), which did not appear obviously to demonstrate maxima behavior, gave results somewhat different than the more dilute Cr(III) concentrations. The scatter in the results grew larger as the Cr(III) concentration was increased over 2 mM. Hence, it was concluded that all data taken at con-

centrations greater than about 1 mM were questionable, and may be demonstrating incipient or overt maxima.

The very dilute Cr(III) concentrations were also not very reliable, because the magnitude of the corrected current was not much greater than the magnitude of the background current. To optimize these two conditions, i.e., freedom from maxima and smallest errors in background current corrections, a Cr(III) concentration of 0.5 mM was chosen. All future work was done with this concentration of Cr(III).

Previous work by Parsons and Passeron[16] had been done on a Cr(III)/Cr(II) system, in $NaClO_4$ medium, at a pH of 3.4. Calculation indicated that at this pH, with a Cr(III) concentration of 5 mM, about half of the reactive species would be in hydrolyzed form. (This is using a hydrolysis constant of log K = -4.01.) This would suggest that the pH in the area of the electrode was essentially undefined, and rendered their rate data suspect. To confirm this suspicion, a series of polarograms was taken in 0.5 F $NaClO_4$, with a Cr(III) concentration of 0.5 mM, with the pH varying from 2.0 to 4.0. The

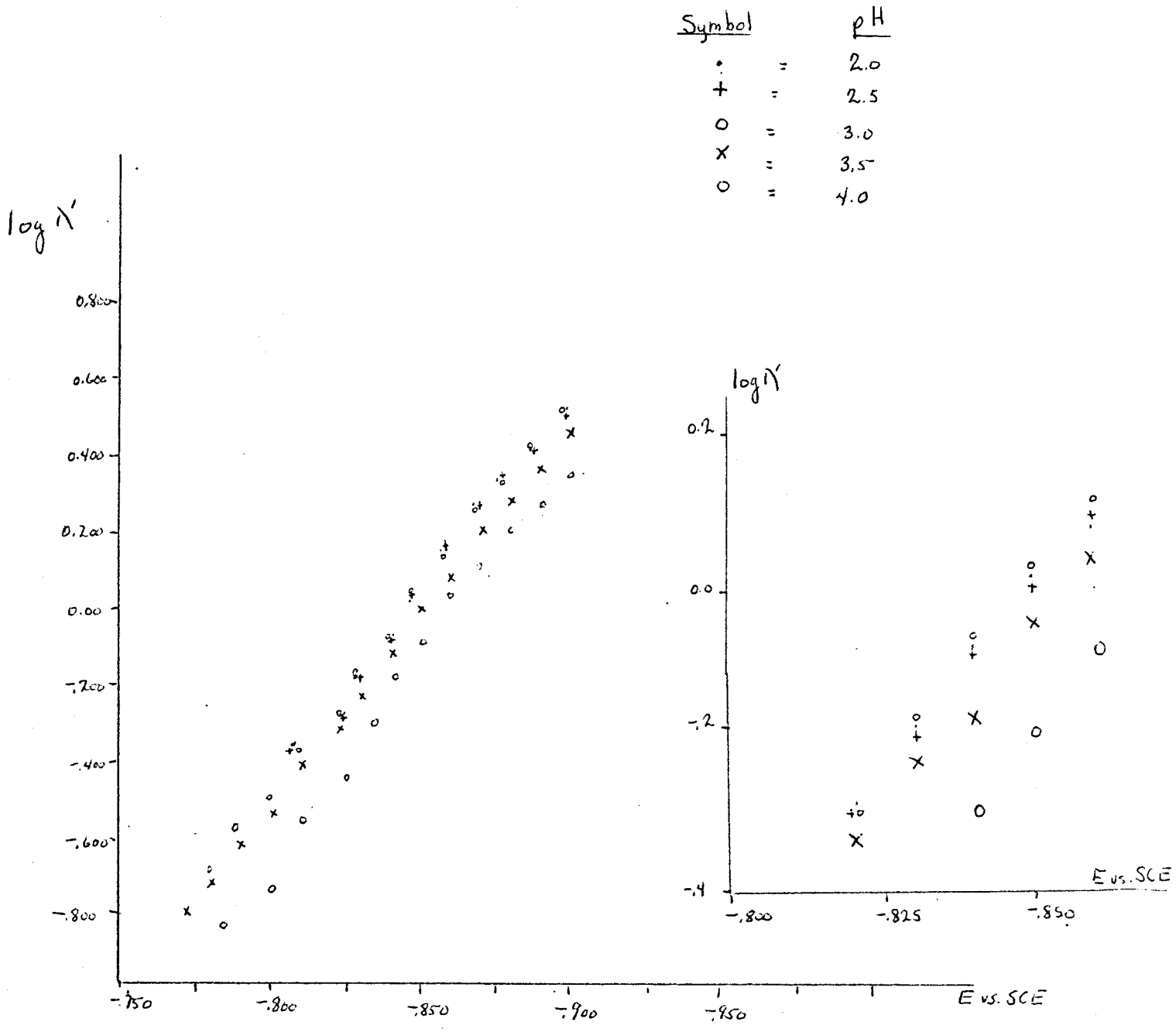

Figure 2. Effect of pH on the polarographic behavior of Cr(III). Data is for 0.5mM Cr(III) in 0.5 F $NaClO_4$, at varying pH.

results are shown in Figure 2. Here it is seen that at a pH of 4.0, the results are divergent from those at more acidic solutions. Also, by a pH of 3.4, the peak heights were becoming irregular and non-reproducible for a given potential. By a pH of 4.0, this was true to such an extent that some amount of arbitrariness was introduced in measuring the polarograms. The more concentrated the Cr(III) solution, the greater the uncertainty in the pH that would be introduced in the electrode area. Parsons and Passeron[16] did not publish the Cr(III) concentration at which they collected their data, but private communication with Passeron indicated this concentration was approximately 5 mM. At a Cr(III) concentration of 5 mM, in a solution of pH 3.4, there are more hydroxyl ions in the hydrolyzed chromium species than there are hydronium ions in solution. The data shown in Figure 2 was taken at a chromium concentration an order of magnitude less than the Parsons and Passeron data. This is perhaps why the data at a pH of 3.4 appears consistent with more acidic pH's, for this low Cr(III) concentration.

To confirm that hydrolysis was substantial for a Cr(III) solution at a pH of 3.4, a pH titration was done, using standard perchloric acid, and a

0.100 F Cr(III) solution, prepared from the mother Cr(III) solution. A blank was run, titrating from a pH of 3.4 to 2.0. The titration was monitored by a Leeds and Northrup pH meter. The response, of course, became relatively insensitive at a pH of 2.0, but within this accuracy the titration of the Cr(III) solution consumed 70% more titrant than the blank, and this excess corresponded roughly to the difference of the hydrolyzed amounts of Cr(III) at a pH of 3.4 and 2.0, respectively (which is nearly equal to the hydrolyzed concentration at a pH of 3.4, because the amount of hydrolyzed Cr(III) at a pH of 2.0 is very small).

All future work was therefore done at a pH of 2.0.

All the data up to this point had been corrected for mass-transfer, but not for double-layer effects. Double-layer theory[22] develops the following equation:

1. $$i = i_t^o \, e^{(\alpha n - z) f \phi_2} \left[e^{-\alpha n f \eta} - e^{(1-\alpha) n f \eta} \right]$$

Where α = transfer coefficient

$f = \mathcal{F}/RT$

ϕ_2 = potential at the outer Helmholtz plane

η = overvoltage

One implication of this equation is that a plot of

log λ (or log k) against potential would not be linear, but would have a potential-dependent slope. By applying an appropriate correction (for the case of the irreversible reaction Cr(III)/Cr(II))

$$\log \lambda_t = \log \lambda - (\alpha - 3)\phi_2 \mathcal{F}/RT$$

one would then expect (if double-layer theory applies) to get a linear plot for log k vs. potential (or overvoltage), only after appropriate double-layer corrections had been made.

However, the Marcus effect would also predict a potential-dependent slope of log k versus overvoltage. Therefore, before an attempt could be made to demonstrate with some confidence whether or not a Marcus effect was operative in this system, reasonable double-layer corrections would have to be made. Correction for double-layer effects, taking into account any specific adsorption, should give a rate constant that would be independent of the concentration or nature of the supporting electrolyte.

To determine if this was indeed the case, a series of polarograms was run using different concentrations of $NaClO_4$. The effect of double-layer corrections would be largest at the more dilute concentrations of supporting electrolyte; hence, it

would be desirable to obtain data at low electrolyte concentration. However, a practical minumum was imposed on how dilute a supporting electrolyte concentration could be used, by the appearance of maxima behavior at low electrolyte concentrations. It was found that concentrations more dilute than 0.3 F $NaClO_4$ could not be used for this reason. The concentrations that were used were: 0.3 F, 0.5 F, 0.7 F, 1.0 F.

Two sets of values for ϕ_2 in perchlorate media were found in the literature: one given by Bockris and coworkers[23] for $NaClO_4$, and one by Parsons and Payne,[24] for $HClO_4$. The slope, $d\phi_2/dE$, was not very different in the two sets of values, but the absolute values for ϕ_2 at a given potential, for a given perchlorate concentration, differed substantially in the two cases.

Both sets of ϕ_2 data were tried. The results for the corrected rate constant function, log Λ, are shown in Table I, for representative potentials. Because of some ambiguities in the data-gathering process as reported by Bockris et. al., and also because of the agreement between the Payne data and similar data gathered by other workers in this lab-

TABLE I

Comparison of Rate Data Obtained in $NaClO_4$ from Two Sets of Values for ϕ_2, The Outer Helmholtz Potential

	Bockris, et. al.[23]				Parsons & Payne[24]			
	Perchlorate Concentrations							
Potential vs. SCE	0.3F	0.5F	0.7F	1.0F	0.3F	0.5F	0.7F	1.0F
-.800 v.								
log Λ'	-.30	-.64	-.77	-.89				
log Λ_t	-2.81	-2.73	-2.64	-2.44	-2.58	-2.33	-2.23	-2.15
-.850 v.								
log Λ'	.22	-.13	-.22	-.31				
log Λ_t	-2.44	-2.31	-2.17	-1.93	-2.19	-1.97	-1.82	-1.73
-.900 v.								
log Λ'	.76	.34	.25	.16				
log Λ_t	-2.01	-1.95	-1.78	-1.51	-1.76	-1.70	-1.51	-1.44
-.950 v.								
log Λ'				.57				
log Λ_t				-1.14				-1.19

$$\log \Lambda' = (12/7)^{\frac{1}{2}} t^{\frac{1}{2}} k_{h,f} D_0^{-\frac{1}{2}}$$

$$\log \Lambda_t = \log \Lambda' - (\alpha - 3)\phi_2 F/RT$$

oratory, it was felt the Payne data was more reliable, and this data was used in the double-layer correction of the perchlorate data. The value of the transfer coefficient, α, changes from the uncorrected log k vs. potential plots to the corrected plots. Therefore, equation 1 was used to evaluate the "true" value of α, by equating the slope

$$\frac{\partial \ln k}{\partial \eta} = -\alpha n f + (\alpha n - z) f \frac{\partial \phi_2}{\partial \eta}$$

(cathodic range).

By determining $\partial \phi_2 / \partial \eta$ (linear over small potential ranges) one could then get a "true" value for α.

It can be seen that the corrected rate constant is not constant for a given potential, for different electrolyte concentrations, as it should be according to double-layer theory.

Therefore, it was decided to collect data in a series of monovalent electrolytes which demonstrated varying amounts of specific adsorption. The series KCl, KBr and KI was chosen. At the potentials used, KCl demonstrates essentially no specific adsorption, and therefore ϕ_2 data for NaF[25] (a monovalent, non-specifically adsorbed electrolyte) was used. The concentrations used were 0.2 F, 0.5 F and 0.8 F KCl.

The ϕ_2 data for KBr was taken from Parsons, Lawrence and Payne.[26] This data was available only for 1.0 F and 0.1 F KBr. However, 0.2 F, 0.5 F and 0.8 F KBr were also studied for comparison with the other halides.

The ϕ_2 data for KI was taken from Breiter et. al.[27] The concentrations of KI were 0.3 F, 0.5 F and 0.8 F.

The results are summarized in Table II. Here it is seen that the double-layer correction for KI applies quite well, in giving internally consistent rate constants for different concentrations of KI, at a given potential. The corrections also apply fairly well in the case of KCl. The corrected data for KBr is somewhat more sketchy, and interpretation is difficult. Agreement between the magnitude of the rate constants for KCl and KI is also fairly good.

Because this data seems to give reasonable double-layer corrections (especially in the case of KI), an analysis of the plots of log k vs. potential was done for this data. Two curves were fit to each data set, using the least-squares criterion of goodness of fit: one was linear (i.e., constant, potential-independent slope) and the second was a second-order expression

TABLE II

Comparison of Corrected & Uncorrected Rate Data for the Potassium Halides

Potential vs. SCE	KCl			KBr					KI		
	0.2F	0.5F	0.8F	0.1F	0.2F	0.5F	0.8F	1.0F	0.3F	0.5F	0.8F
-0.750 v.											
log Λ'	-.90			-.23	-.71				-.82	-.76	-.72
log Λ_t	-3.09			-3.18					-3.46	-3.46	-3.48
-0.800 v.											
log Λ'	-.18	-.77		.45	-.11	-.58	-.68	-.70	-.79	-.73	-.69
log Λ_t	-2.60	-2.53		-2.68				-2.38	-2.95	-2.92	-2.98
-0.850 v.											
log Λ'	.41	-.22	-.48		.43	-.07	-.22	-.24	-.76	-.70	-.66
log Λ_t	-2.21	-2.14	-2.13					-1.92	-2.39	-2.42	-2.45
-0.900 v.											
log Λ'	1.00	.28	.04		.99	.40	.23	.19		-.67	
log Λ_t	-1.80	-1.81	-1.78					-1.51		-1.83	

$$\log \Lambda' = (12/7)^{\frac{1}{2}} t^{\frac{1}{2}} k_{h,f} D_0^{-\frac{1}{2}}$$

$$\log \Lambda_t = \log \Lambda' - (\alpha - 3)\phi_2 F/RT$$

of the type: $\ln k = a_o + a_1\eta + a_2\eta^2$ (potential-dependent slope). The second order coefficient, a_2, then gave the magnitude of the potential-dependence of the curve. The results are summarized in Table III. It should be noted that $\eta = E-E_o'$, following the notation of Marcus theory. A value of -0.641 v. vs. SCE was used for E_o'.[28]

Thus it is seen that for two monovalent electrolytes, KCl and KI, it is possible to obtain reasonable double-layer corrections (KBr is doubtful); while for another monovalent electrolyte, $NaClO_4$, the double-layer theory does not seem to yield satisfactory results.

Asada, Delahay and Sundaram[29] suggest that the failure of the double-layer theory is to be expected for mixtures of electrolytes with different ionic valences because of local variations of potential in the plane of closest approach. This effect they call the local field effect, and arises because the Poisson equation is solved for only one dimension, and hence does not take into account variations of potential in planes <u>parallel</u> to the electrode. They publish data for the discharge of Ga^{+3} on mercury in perchlorate media; the double-layer corrections

TABLE III

Potential-Dependent and Potential-Independent Slopes for Potassium Halides

	KCl				KBr				KI			
	Concentration (formality)	A_o* (Linear)	A_1**	A_2**	Concentration	A_o (Linear)	A_1	A_2	Concentration	A_o (Linear)	A_1	A_2
Data corrected for double-layer	0.2	.47	.59	.60	0.1	.56	.32	-2.02	0.3	.61	.58	-.25
	0.5	.41	.58	.72					0.5	.60	.60	0.00
	0.8	.43	.54	.41					0.8	.61	.54	-.47
					1.0	.63	.38	-1.16				
Data uncorrected for double-layer					0.1	.77	.76	-.28				
	0.2	.70	.92	1.15	0.2	.65	.71	.29	0.3	.46	.44	-.18
	0.5	.60	.86	1.14	0.5	.54	.67	.55	0.5	.44	.43	-.11
	0.8	.58	.79	.83	0.8	.51	.59	.34	0.8	.48	.37	-.71
					1.0	.52	.40	-.57				

* $\alpha = A_o$

** $\alpha = A_1 + A_2\eta$

fail for the univalent and divalent salts (Na^+ and Mg^{++}) but hold for the trivalent salt (Al^{+++}). Furthermore, the Mg^{++} salt double-layer correction is better than the Na^+ salt double-layer correction.

It was therefore decided to collect data for the Cr(III)/Cr(II) system, using a trivalent electrolyte. $Al(ClO_4)_3$ was chosen, to permit comparison with $NaClO_4$, where the double-layer correction failed.

Some difficulty was experienced in solution preparation, because of the slow hydrolysis of aluminum in perchlorate medium (See Experimental, p. 6). To facilitate comparison with the sodium perchlorate data, the same ionic strengths were used for the aluminum salt as had been used for the sodium salt: 0.0500 F ($\mu = 0.3$), 0.0833 F ($\mu = 0.5$), 0.1167 F ($\mu = 0.7$) and 0.1667 F ($\mu = 1.0$).

To get ϕ_2 data for $Al(ClO_4)_3$, the Joshi-Parsons equation:[30]

$$q^m = \pm\ 2(kT\varepsilon/8\pi)^{\frac{1}{2}} \left\{\Sigma\, n_i(u_2^{2i}-1)\right\}^{\frac{1}{2}}$$

where q^m = charge on electrode

ε = dielectric constant

n_i = concentration of ions of species in the bulk of the solution

$u_2 = \exp(-e_o\phi_2/kT)$

e_o = charge on electron

was used. The indicated numerical integration was performed in a Citran program to generate a series of values of q^m vs. ϕ_2 for the desired $Al(ClO_4)_3$ concentrations. The assumption was then made that there was no perchlorate adsorption at the potentials of interest (-0.800 v. to -1.050 v. vs. SCE). Data for q^m vs. ϕ_2 was then available from Russell for a monovalent electrolyte[31] (NaF). Then, the aluminum data was compared to Russell's tables for a given ionic strength; for a given charge on the electrode, a $\Delta\phi_2 = \phi_2\ Al(ClO_4)_3 - \phi_2\ NaF$ could be found. It was assumed that this difference in $\Delta\phi_2$ could be equated to the difference ΔE for the two electrolytes. This then gave a series of values of ϕ_2 vs. E for $Al(ClO_4)_3$. This calculation is summarized in Figure 3.

The resulting data analysis for $Al(ClO_4)_3$ is given in Table IV. The $NaClO_4$ data is also presented for comparison.

It can be seen that the rate constants at a given potential are reasonably constant for different aluminum concentrations. However, these corrected constants for aluminum differ substantially from those of $NaClO_4$; it can also be seen that the rate

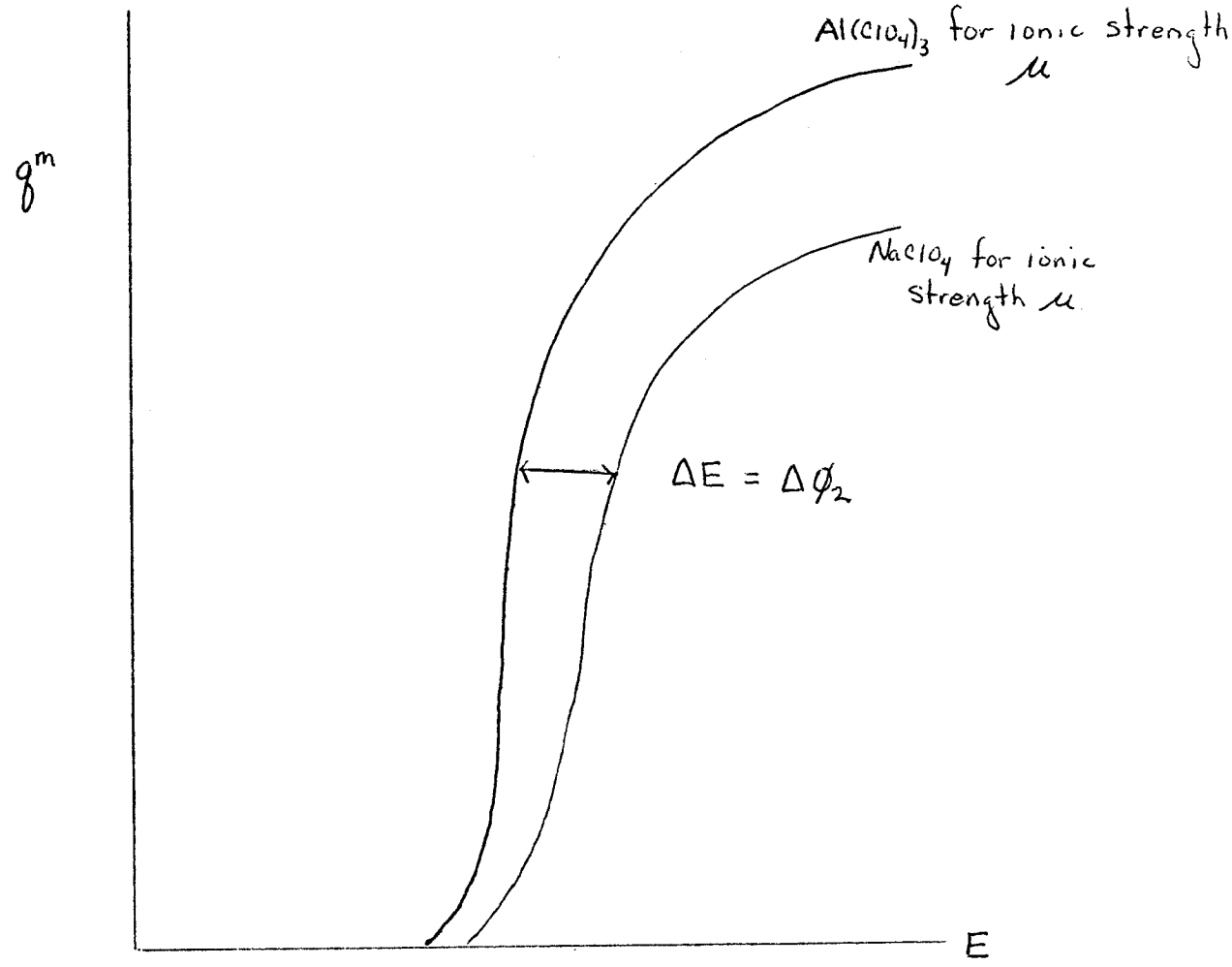

Figure 3. Calculation of ϕ_2 potentials vs. potential for $Al(ClO_4)_3$.

TABLE IV

Corrected and Uncorrected Rate Data for $Al(ClO_4)_3$ and $NaClO_4$

	$Al(ClO_4)_3$				$NaClO_4$			
Concentration (formality)	.0500	.0833	.1167	.1667	0.3	0.5	0.7	1.0
Ionic Strength	0.3	0.5	0.7	1.0				
-.800 v.								
log Λ'	-.74				-.30	-.64	-.77	-.89
log Λ_t	-2.07				-2.58	-2.33	-2.23	-2.15
-.850 v.								
log Λ'	-.24	-.48	-.52	-.65	.22	-.13	-.22	-.31
log Λ_t	-1.62	-1.71	-1.64	-1.67	-2.19	-1.97	-1.82	-1.73
-.900 v.								
log Λ'	.25	.07	0.00	-.10	.76	.34	.25	.16
log Λ_t	-1.20	-1.22	-1.18	-1.17	-1.76	-1.70	-1.51	-1.44
-.950								
log Λ'	.716	.60	.49	.36				.57
log Λ_t	-.79	-.74	-.74	-.75				-1.19

*$\log \Lambda' = (12/7)^{\frac{1}{2}} t^{\frac{1}{2}} k_{f,h} D_0^{-\frac{1}{2}}$

**$\log \Lambda_t = \log \Lambda' - (\alpha - 3)\phi_2 F/RT$

constants in aluminum are considerably larger than those in the halides, by .5 to .8 log units.

Curve-fitting analysis was also done on the $Al(ClO_4)_3$ and $NaClO_4$ data. The same procedure was followed as for the halide series, and the results are presented in Table V. These results indicate that the curvature of the ln k vs. potential plots increase with increasing concentration. It is possible, through Marcus theory, to obtain an estimate of the magnitude of the second-order coefficient.

The equation

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{Y}{4} + \frac{n\mathcal{F}\eta}{2} + \frac{(n\mathcal{F}\eta + w^p - w^r)^2}{4Y}$$

was presented in the Introduction. If one corrects for double-layer effects, w^p and w^r will be zero. One then obtains (with n = 1)

$$\Delta F^* = \frac{Y}{4} + \frac{F\eta}{2} + \frac{(F\eta)^2}{4Y}$$

If the potential is at the equilibrium potential, the overvoltage is zero; if internal contributions to the entropy of the system during reaction are neglected, one can equate the $\Delta F^*_{eq} = \frac{Y}{4}$ (at $\eta = 0$) to the experimental heat of activation, $\Delta H^*_{app} = \frac{Y}{4}$.

The transfer coefficient then becomes

$$\alpha = \frac{\partial \Delta F^*}{F\,\partial\eta} = \frac{1}{2} + \frac{F\eta}{2Y} = \frac{1}{2} + \left(\frac{F}{8(\Delta H^*_{app})}\right)\eta$$

TABLE V

Potential-Dependent and Potential-Independent Slopes for Aluminum and Sodium Perchlorate

		$Al(ClO_4)_3$			$NaClO_4$		
	Concentration (ionic strength)	A_o* (Linear)	A_1**	A_2**	A_o* (Linear)	A_1**	A_2**
Data corrected for double-layer	0.3	.49	.49	-.01	.49	.59	.49
	0.5	.56	.46	-.37	.35	.59	1.09
	0.7	.55	.81	1.05	.39	.88	2.28
	1.0	.53	.87	1.29	.33	.67	1.38
Data uncorrected for double-layer	0.3	.56	.59	.14	.63	.84	1.04
	0.5	.63	.60	.15	.56	.73	.81
	0.7	.61	.89	1.08	.55	.99	1.99
	1.0	.58	.96	1.41	.50	.94	1.70

* $\alpha = A_o$

** $\alpha = A_1 + A_2\eta$

Evaluation of ΔH^* would then allow one to calculate the second-order coefficient, $\left(\frac{F}{8(\Delta H^*)}\right)$. If one obtains rate data at different temperatures, the slope $\frac{d \ln k}{d(\frac{1}{T})}$ may be used for calculation of the apparent heat of activation, ΔH^*_{app}. The apparent heat of activation is obtained because double-layer corrections are not available for the desired $NaClO_4$ or $Al(ClO_4)_3$ concentrations at different temperatures. Also, there seems to be a dearth of reliable data on the temperature coefficient of the standard potential of this couple. It appears from previous calculations[32] that the true heat of activation is higher than the apparent value.

Rate data was obtained at different temperatures (25°, 35°, 45°) for $NaClO_4$, KI and $Al(ClO_4)_3$. A heat of activation was found for $NaClO_4$, even though the double-layer corrections failed, for comparison with Parsons and Passeron's data. KI and $Al(ClO_4)_3$ were chosen because the double-layer corrections appeared to apply for these two electrolytes. The graphs of $\log \Lambda'$ vs. $(1/T)$ for these three electrolytes are shown in Figure 4. The apparent heats of activation, and predicted second-order coefficients, are shown

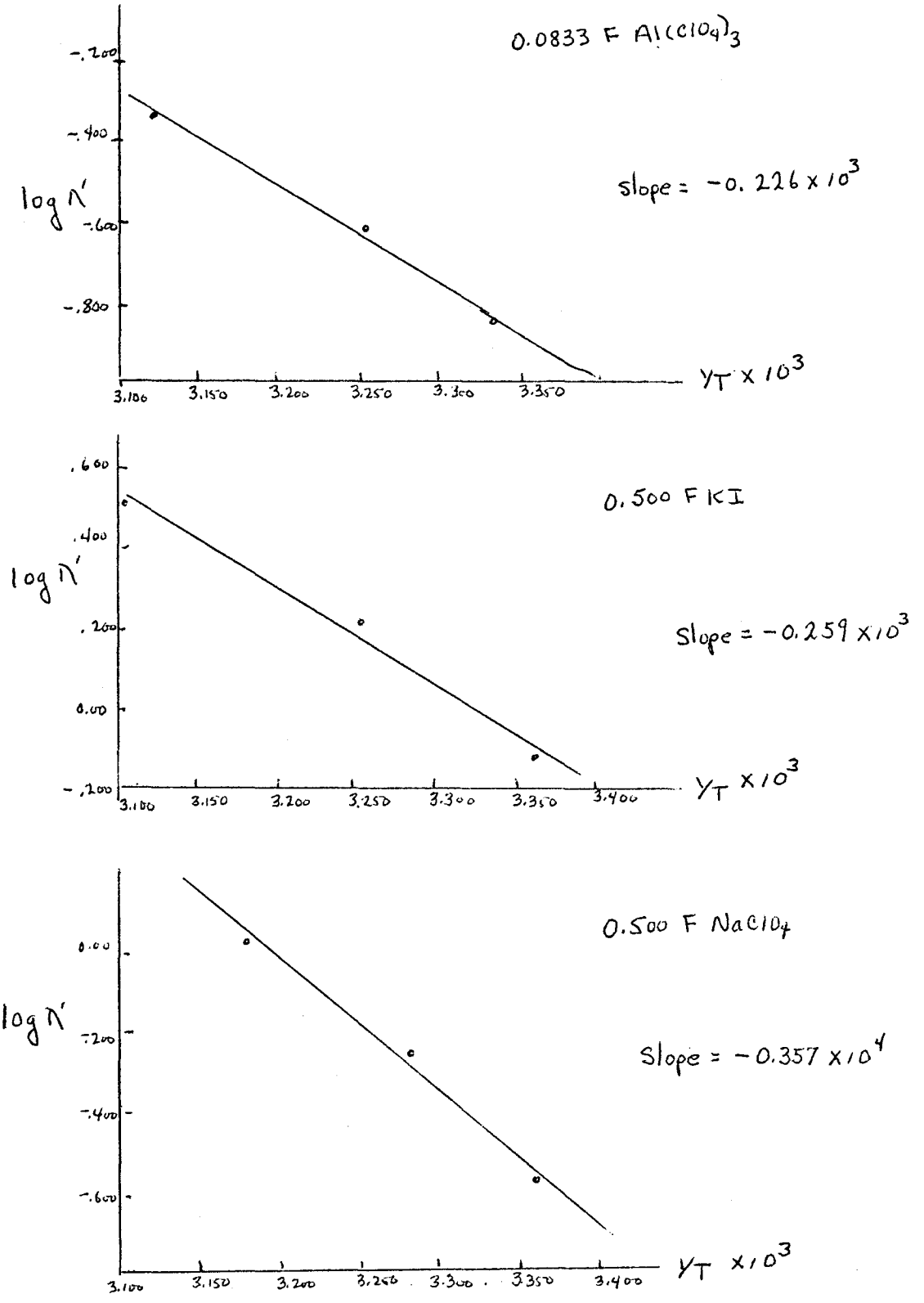

Figure 4. Rate constants at various temperatures for 0.0833 F $Al(ClO_4)_3$, 0.5 F KI, and 0.5 F NaClO. Slopes are used to calculate ΔH^*_{app}.

in Table VI. Two notations are used, $\Delta H'_{app}$, and ΔH^*_{app}.

ΔH^*_{app} = Apparent heat of activation at the standard potential.

$\Delta H'_{app}$ = Apparent heat of activation at a given potential.

It is desirable to use ΔH^*_{app}; however, $\Delta H'_{app}$ is the quantity directly obtained from the Figure 4. The two are related as follows:

$$\Delta H^*_{app} = -R \left(\frac{\partial \ln k_s}{\partial (1/T)}\right)$$

Where $k_s = k_c^o \exp(-\alpha n \mathcal{F} \mathcal{E}'_o / RT)$

$\mathcal{E}'_o$ = standard potential referred to SCE

$$\ln k_s = \ln k_c^o - \left(\frac{\alpha n \mathcal{F} \mathcal{E}'_o}{RT}\right);$$

$$\ln k_c = \ln k_c^o - \left(\frac{\alpha n \mathcal{F} \mathcal{E}}{RT}\right)$$ where k_c is the rate constant at potential $\mathcal{E}$.

$$\ln k_s - \ln k_c = \frac{-\alpha n \mathcal{F}}{RT} (\mathcal{E}'_o - \mathcal{E})$$

$$\frac{\partial (\ln k_s)}{\partial (1/T)} = \frac{\partial (\ln k_c)}{\partial (1/T)} \frac{-(\alpha n \mathcal{F})}{R} (\mathcal{E}'_o - \mathcal{E})$$

This implies $\frac{\partial (\mathcal{E}'_o - \mathcal{E})}{\partial (1/T)} = 0$, for a range of 20°.

Then $\Lambda' = \left(\frac{12}{7}\right)^{\frac{1}{2}} t^{\frac{1}{2}} k_c D_0^{-\frac{1}{2}}$

$$\ln \Lambda' = \ln k_c + \ln \left[\left(\frac{12}{7}\right)^{\frac{1}{2}} t^{\frac{1}{2}} D_0^{-\frac{1}{2}}\right]$$

$$\frac{\partial \ln \Lambda'}{\partial (1/T)} \cong \frac{\partial \ln k_c}{\partial (1/T)}$$

$$\Delta H^*_{app} = -R \left(\frac{\partial \ln k_s}{\partial (1/T)}\right) = -R \left[\frac{\partial (\ln \Lambda')}{\partial (1/T)} - \frac{(\alpha n \mathcal{F})}{R} (\mathcal{E}'_o - \mathcal{E})\right]$$

TABLE VI

	$NaClO_4$	KI	$Al(ClO_4)_3$	$NaClO_4$ Parsons & Passeron[16]
$\Delta H'_{app}$	16.3 kcal	1.19 kcal	1.03 kcal	
(potential-dependent)	(-.800 v vs SCE)	(-.750 v.)	(-.800 v.)	
ΔH^*_{app}	18.1 kcal	3.62 kcal	2.82 kcal	11 kcal
$Y = 4 \Delta H^*_{app}$	72.4 kcal	14.5 kcal	11.3 kcal	44 kcal
Second-order Coefficient, A_2 $A_2 = \frac{\mathcal{F}}{2Y}$	0.16	0.79	1.00	0.26

DISCUSSION

To determine clearly whether Marcus theory is correct in predicting a potential-dependence of α, it is necessary to have a well-behaved system where the double-layer theory appears to yield satisfactory results. Otherwise, it would be impossible to determine whether any curvature in a log k vs. η plot was due to failure of the double-layer correction, some idiosyncrasy of that particular system, or indeed to the type of effect Marcus theory would predict.

Because of the previous work done by Parsons and Passeron,[16] data were first obtained in $NaClO_4$ media. However, the double-layer corrections failed in this case. Nevertheless, the data were analyzed for second-order potential-dependence, to permit comparison with the results of Parsons and Passeron. The magnitude of second-order coefficient, A_2, changed with $NaClO_4$ concentration. The result for 0.5 F $NaClO_4$ (the concentration used by Parsons and Passeron) was $A_2 = 1.09$, compared to a value of 0.26 obtained by Parsons and Passeron.

There are several reasons why the data obtained by Parsons and Passeron may differ from the results of the work. First, they used a pH of 3.4. As the

pH study on Cr(III) indicated, the Cr(III) system is relatively sensitive to pH, and at a pH of 3.4 sufficient hydrolysis may take place to render the pH in the vicinity of the electrode indeterminate. Secondly, Marcus theory defines the overvoltage as $\eta = E-E_o'$, where E_o' is the standard potential referred to some convenient reference potential (usually the potential of the SCE). However, in their work Parsons and Passeron apparently used the conventional overvoltage, $\eta = E-E_{rev}$, where E_{rev} is the equilibrium potential for a given concentration of oxidized and reduced species. The overvoltage as used in Marcus theory would then correspond to the overvoltage used by Parsons and Passeron only in that case where the concentrations of oxidized and reduced species were equal, i.e., where $E_o' = E_{rev}$.

This work used the Marcus theory overvoltage, i.e., $\eta = E-E_o'$. Because Parsons and Passeron did not publish the concentrations of Cr(III) and Cr(II) with which they were working, it is therefore not possible to convert their data to a form which would be strictly comparable to the data obtained in this work.

One of the impressive correlations obtained by

Parsons and Passeron was the agreement between the experimental second-order coefficient, A_2, and an estimate of that coefficient predicted by Marcus theory, by equating the apparent heat of activation to ΔF^*_{eq}. No such correlation was obtained in this work. The coefficient predicted from Marcus theory and ΔH^*_{app} was 0.16; the experimental second-order coefficients were all considerably larger than this, ranging from 0.49 for 0.3 F $NaClO_4$ to 1.38 for 1.0 F $NaClO_4$. However, even if agreement had been obtained, little faith could be placed in it, because the double-layer corrections failed. A skeptic might then claim that any curvature resulted from this failure, and that agreement with predictions of Marcus theory was simply fortuitous.

There is no way to decide if double-layer corrections did apply for the data of Parsons and Passeron, because this data was collected for only one $NaClO_4$ concentration. Also, the high pH used in their work, and the use of an inappropriate definition of overvoltage, makes it difficult to assess the significance of their agreement between A_2 from curve analysis and A_2 predicted by Marcus theory.

In an attempt to find a system where reasonable

double-layer corrections could be made, a series of potassium halides was run: KI, KBr, KCl. For KI, the double-layer corrections held strikingly well; for KCl, the corrections were also good. Double-layer data could only be found for 0.1 and 1.0 F KBr. There was little overlap between the data at these two concentrations, so it is difficult to determine the extent to which the double-layer corrections applied. The rate constant obtained in KCl differed by no more than 0.4 log units, at a given potential, from that obtained for KI.

Neglecting KBr for the moment, here are then two electrolytes in which one would look for the presence or absence of potential-dependence of α with some confidence in its significance. The KCl data do seem to demonstrate curvature, implying a potential-dependence of α. Furthermore, using a weighted error function as a measure of goodness of fit, the second-order curves fit the data better than linear ones.

Again, however, the magnitude of the second-order coefficient seems to vary with concentration of electrolyte. In the case of KCl, I do not believe this variation is significant. These data were anal-

yzed for several different sets of points; including or excluding a few points at each end of the curve resulted in a variation of the second-order coefficient, for a given concentration, of about the order observed for the variation of A_2 among different KCl concentrations. Each electrolyte concentration covered a slightly different number of points; because of the shift of the half-wave potential with electrolyte concentration, different ranges were covered before reaching the hydrogen wave. Essentially, what one does by fitting a second-order equation to these points is to fit a section of a parabola; and it is obvious that the coefficients involved will be a fairly sensitive function of which section is chosen.

Thus, the fact that the KCl data do appear to demonstrate second-order potential-dependence seems clear, although no great confidence should be placed in the quantitative values for this dependence.

The KI data are somewhat more ambiguous. First, the sign of the second-order potential-dependence is different than for either KCl or $NaClO_4$. Also, the potential-dependence is not as large as that for KCl. The largest potential-dependence is shown by

0.8 F KI; however, this is the one data set for which the weighted error function indicates a better fit with a linear curve than with a second-order curve.

The 0.5 F KI data shows no curvature, and the curvature of the 0.3 F KI data is small. Furthermore, the magnitude of the linear constant (i.e., potential-independent α) is indeed constant for all three concentrations. There thus seems to be little justification for invoking any Marcus effect with this data; it fits very well into the assumption that α is potential-independent.

Because the KI data also demonstrates the best double-layer corrections, one might be tempted to relate apparent second-order potential-dependence with failure of double-layer theory rather than any Marcus effect. However, it should be pointed out that the rate constants, uncorrected for double-layer, of the different KI concentrations differ very little. Also, $\frac{d\phi_2}{d\eta}$ for KI is very small. Thus, one would expect the absolute error in double-layer corrections to be small, because the data is already so similar for different KI concentrations. The corrected KI data may look good not because double-

layer theory held so well here, but because there was not much test of double-layer theory. Any correlation based on the KI data between the applicability of double-layer theory, and apparent second-order potential-dependence, would therefore be somewhat tenuous.

The experimental heat of activation data, according to approximations made from Marcus theory, would predict a large second-order coefficient for KI (0.79). This is rather remarkable, in view of our earlier conclusion that the KI data does not justify a potential-dependent α. The plot used to evaluate ΔH^*_{app} was based on only three points, and the deviation of these points from the best line was appreciable. This data is therefore not completely reliable. Even so, the experimental error is not great enough to explain a difference of this magnitude between predicted and experimental results. One explanation is that the assumptions involved are faulty (e.g., that the entropy term can be neglected, and $\Delta F_{eq} = \Delta H^*_{app}$). Also, this could be interpreted as evidence against the validity of Marcus theory.

The $Al(ClO_4)_3$ study was undertaken to test the

significance of the local field effects cited by Delahay et. al.[29] Certainly, the $NaClO_4$ double-layer corrections did fail; and if they failed because of local field effects, $Al(ClO_4)_3$ should give satisfactory double-layer corrections. The double-layer corrections did hold for $Al(ClO_4)_3$. However, there are some disturbing elements in these data. First, the rate constants, after double-layer correction, are significantly higher in $Al(ClO_4)_3$ than in the other electrolytes, for a given potential. It was mentioned earlier that the slow hydrolysis of aluminum in perchlorate media was a problem; although precautions were taken to overcome this problem, it may be that this slow equilibrium was still in some way affecting the data. It has been shown that the polarographic behavior of Cr(III) is affected by pH, in certain ranges; and it may be that in $Al(ClO_4)_3$ the Cr(III) data is in some way anomalous.

However, even if this is not the case, local field effects seem inadequate to explain why the double-layer corrections apparently failed for $NaClO_4$, and apparently held for $Al(ClO_4)_3$. For two monovalent electrolytes, KCl and KI, the double-layer corrections applied reasonably well; the local field

effects which were present in $NaClO_4$ should also be present in these electrolytes.

It perhaps might have been interesting to try a divalent electrolyte. If one could duplicate Delahay's result, i.e.; if the double-layer correction was intermediate for the case of a divalent electrolyte, for the Cr(III) system, this would tend to confirm the importance of local field effects, in spite of the halide data.

Because the double-layer correction did seem to apply for $Al(ClO_4)_3$, an analysis of possible potential-dependence of α was also done here. Once again, the second-order coefficient appeared to be dependent on the concentration of $Al(ClO_4)_3$, this time in a monatonic fashion. The sign change at 0.0833 F $Al(ClO_4)_3$ is interesting, but may not be significant, for the reasons given in connection with the KCl and KI data.

The apparent heat of activation was low, 2.82 kcal; this, when used with Marcus theory, led to a prediction of 1.00 for a second-order coefficient. The heat of activation studies were done on 0.0833 F $Al(ClO_4)_3$; comparison with the experimental second-order coefficient at this concentration of $Al(ClO_4)_3$ (-0.37) shows little correlation. Again, this would

seem to imply that either the assumptions about neglecting the entropy term are false, or else that this is evidence against the Marcus theory. Another possibility is that the data itself cannot be simply interpreted because of the hydrolysis problem.

The standard rate constant, available from the apparent heat of activation for $Al(ClO_4)_3$, would appear to be anomalously low. However, double-layer corrections would have the effect of increasing the rate data, by a factor of about 2 $\log_{10}$ units; it is likely that the true heat of activation would be higher than that of the apparent value. This would help explain the abnormally low standard rate constant that would be calculated from the given apparent heat of activation for $Al(ClO_4)_3$.

However, the standard rate constant for $NaClO_4$ and $Al(ClO_4)_3$ would still not be in agreement, by a factor of about 1.5 $\log_{10}$ units, even after double layer corrections. This may indicate that the $Al(ClO_4)_3$ heat of activation data is suspect, possibly for reasons already mentioned in connection with the $Al(ClO_4)_3$ data.

It should perhaps be pointed out here that determining a potential-dependence of α has considerable importance, apart from any implications about Marcus

theory.

It may also be that, if α is potential-dependent, the relationship may not be the simple $\alpha = a_1 + a_2\eta$ one predicted by Marcus theory. A more complex relation could perhaps account for the seemingly regular variation of the potential-dependent coefficient with concentration of electrolyte.

SUMMARY

The $NaClO_4$ data was shown to disagree with previous data for $NaClO_4$ published by Parsons and Passeron[16]. A variety of reasons for this discrepancy was suggested. Because the double-layer corrections failed for $NaClO_4$, no significant conclusions could be drawn from this work about the validity of Marcus theory predictions.

Three electrolytes were investigated for which double-layer corrections did apply fairly well: KCl, KI and $Al(ClO_4)_3$. The KI data seemed to fit the assumption of a potential-independent α.

The KCl and $Al(ClO_4)_3$ data both seemed to imply a potential-dependence of α. However, no quantitative agreement was found between Marcus theory predictions and the magnitude of the potential-dependent coefficient.

The local field effect, suggested by Delahay *et. al.*[29] for the failure of double-layer corrections in the case

of mixed electrolytes, does not seem adequate to explain the failure of double-layer corrections for $NaClO_4$.

REFERENCES

1. Delahay, P., "Double Layer and Electrode Kinetics," New York: Interscience Publishers, 1965, pp. 153-177.

2. Van Rysselberghe, Electrochim. Acta, 8 (1963) 583, 709.

3. Marcus, R. A., J. Chem. Phys., 43 (1965) 679.

4. Marcus, R. A., J. Chem. Phys., 24 (1956) 966.

5. Marcus, R. A., Can. J. Chem., 37 (1959) 155.

6. Marcus, R. A., Trans. Symp. Electrode Processes, Phila., Pa., 1959, 239-245 (1961).

7. Marcus, R. A., J. Phys. Chem., 67 (1963) 853.

8. Marcus, R. A., Ann. Rev. Phys. Chem., 15 (1964) 155.

9. Y appears as λ in Marcus' papers. This change of notation has been made to avoid confusion with Λ introduced by the Koutecky analysis.

10. Marcus, R. A., op. cit., Can. J. Chem., p. 156.

11. Hunt, J. P. and H. Taube, J. Chem. Phys., 19 (1951) 602; ibid., 18 (1950) 757.

12. Randles, J. E. B. and K. W. Somerton, Trans. Faraday Soc., 48 (1952) 937.

13. Delahay, P., "New Instrumental Methods in Electrochemistry," New York: Interscience Publishers, 1954, especially Chapter 4.

14. Vetter, K. J., "Electrochemical Kinetics," New York: Academic Press, 1967.

15. Delahay, op. cit., "New Methods...", p. 79.

16. Parsons, R. and E. Passeron, J. Electroanal. Chem., 12 (1966) 524.

17. Delahay, op. cit., "New Methods. . .," p. 79.

18. Ives, D. J. G. and G. J. Janz, "Reference Electrodes: Theory and Practice," New York: Academic Press, 1961.

19. Altman, C. and E. L. King, JACS, 83 (1961) 2825.

20. Aveston, J., J. Chem. Soc. (London), (1965) 4438.

21. Sillen, L. G., Quart. Rev., 13 (1959) 146.

22. Delahay, op. cit., "Double Layer. . .", pp. 199-201.

23. Wroblowa, Kovac and Bockris, Trans. Faraday Soc., 61, (1965) 1523.

24. Parsons, R. and R. Payne, mentioned in Reference 16 as unpublished data.

25. Russell, J. Electroanal. Chem., 6 (1963) 486.

26. Lawrence, Parsons and Payne, J. Electroanal. Chem., 16 (1968) 193.

27. Breiter, M., M. Kleinerman and P. Delahay, JACS, 80 (1958) 5115.

28. Charlot, M., "Selected Constants: Oxidation-Reduction Potentials," New York: Pergamon Press, 1954.

29. Asada, K., P. Delahay and A. K. Sundaram, JACS, 83 (1961) 3398.

30. Joshi, K. M. and R. Parsons, Electrochim. Acta, 4 (1961) 129.

31. See Reference 25.

32. Joshi, K. M., W. Mehl and R. Parsons, Transactions of the Symposium on Electrode Processes, Philadelphia, 1959, edited by E. Yeager, New York: Wiley, 1961.