

A value of $-\Delta F^\circ$ ($= 2400$ cal. at 25°) has already been calculated in the text from measurements of the dissociation constant at various temperatures. The magnitude of $\Delta F^{H/T}$ can be computed from the rate coefficient ratio k_2^H/k_2^D by the utilization of eq. 12 linking the tritium and deuterium isotope effects

$$k_2^H/k_2^T = (k_2^H/k_2^D)^{1.442}$$

The data for azulene give a value of $k_2^H/k_2^T = 12$, which corresponds to a $\Delta F^{H/T}$ of 1500 cal. Thus, $\Delta F_2^* = \Delta F_1^* - 900$ cal. and $\Delta F_{-1}^* = \Delta F_1^* - 2400$ cal. These values when substituted in eq. 14 lead to eq. 12.

Equations 15 and 16 can be used to compute the free energies for the component steps of the detritiation reaction. Substituting in eq. 14 with values of $\Delta F_2^* = \Delta F_1^* - 900$ cal. and $\Delta F_{-1}^* = \Delta F_1^* - 2400$ cal. and evaluating the numerical exponential terms, it is found that

$$\Delta F_1^* = \Delta F_{EX}^* - 2.65RT \quad (17)$$

The numerical values of ΔF_{-1}^* , ΔF_2^* , and ΔF_1^* evaluated from the observed free energy of activation via eq. 15–17, respectively, are as follows: $\Delta F_1^* = 17.5$, $\Delta F_{-1}^* = 15.1$, and $\Delta F_2^* = 16.6$ kcal. mole $^{-1}$.

Hydrogen, Rhodium, and Iridium Electrode Potentials in Lithium Chloride–Potassium Chloride Eutectic

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Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received November 12, 1964

A hydrogen electrode suitable for use in anhydrous molten LiCl–KCl at 450° was prepared by bubbling mixtures of purified hydrogen and hydrogen chloride over a platinized platinum flag immersed in the melt. The potential of this electrode with respect to platinum foils in contact with platinum(II) was measured. Values of free energy, enthalpy, and entropy for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ calculated from the potentials of the hydrogen and chlorine electrodes were in agreement with N.B.S. and JANAF values. Standard potentials were also determined for rhodium(III)–rhodium and iridium(III)–iridium.

Several publications^{3–6} have established an electromotive force series in anhydrous, molten LiCl–KCl eutectic at 450°. Standard potentials were determined for metal ion–metal, metal ion–metal ion, and halogen–halide ion couples with reference to the electrode Pt(II) (1.0 M)–Pt. In this paper the preparation of a hydrogen electrode of the type HCl(g)–H₂(g), Pt suitable for use in this melt is discussed, and its standard potential with respect to Pt(II) (1.0 M)–Pt is determined. Standard potentials for Rh(III)–Rh and Ir(III)–Ir were also determined.

Delimarskii and Markov⁷ have included the hydrogen electrode in their extensive review of reference electrodes for fused-salt media. Their discussion, however, is

concerned with electrodes of the type H₃O⁺–H₂(g), Pt. Several French workers have recently studied^{8–12} current–potential curves obtained in molten LiCl–KCl eutectic contaminated with OH[–] or O^{–2} using a hydrogen gas electrode and have interpreted them on the basis of reactions involving O^{–2}, OH[–], H₂O, and H₃O⁺; additions of O^{–2} and OH[–] were made, and their effects were studied. Pizzini and co-workers^{13,14} have made studies of hydrogen evolution from molten, moist potassium difluoride, and Shams el Din¹⁵ has studied hydrogen evolution in molten KHSO₄. The experimental data for a hydrogen electrode of the type HCl(g)–H₂(g), Pt, obtained in a study of aqueous contamination of equimolar NaCl–KCl at 700° by Littlewood and Argent,¹⁶ in a melt presumably containing little or no O^{–2} or OH[–], were interpreted by these authors as indicating that equilibrium was not achieved. In this study, reversible behavior has been observed for a hydrogen electrode of the latter type under scrupulously anhydrous conditions.

Standard potentials of rhodium(III) have been determined in molten alkali sulfates by Liu¹⁷ and by Johnson and Laitinen.¹⁸ Iridium has not previously been studied in fused salts. Additional references on electrode potentials in fused-salt media can be found in a recent review.¹⁹

(1) Sponsored in part by the Army Research Office, Durham, N. C.; abstracted from the Ph.D. thesis of J. A. Plambeck, 1965.

(2) Argonne National Laboratory, Lemont, Ill.

(3) H. A. Laitinen and C. H. Liu, *J. Am. Chem. Soc.*, **80**, 1015 (1958).

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(18) K. E. Johnson and H. A. Laitinen, *J. Electrochem. Soc.*, **110**, 314 (1963).

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Materials and Equipment

Equipment. Potential measurements were made with a Type K-3 universal potentiometer (Leeds and Northrup Co., Philadelphia, Pa.). Voltammetric measurements utilized a Model XV polarograph, and coulometric generation of metal ions was carried out with a Model IV coulometric current source (E. H. Sargent and Co., Chicago, Ill.). The split-tube furnace used has been described previously.¹⁸ The electrolytic cell used was similar to that described previously,⁴ except that the crucible containing the melt was not part of the outer atmosphere envelope but fitted within it. The hydrogen-electrode assembly, similar to that used by Pankey⁴ for the chlorine electrode, employed standard taper ground-glass joints instead of rubber seals, and a platinum flag welded to a platinum wire, sealed through glass at the top of the electrode assembly, replaced the graphite rod. The cell, outer envelope, hydrogen-electrode assembly, electrode-isolation compartments, and gas-purification trains were constructed of Pyrex (Corning 774). Medium-porosity, sintered-glass sealing tubes (Corning 10 M) were used in the hydrogen-electrode assembly and electrode-isolation compartments. All portions of this glassware coming in contact with the molten salt were boiled in HClO₄, rinsed in deionized water, and dried for several hours at 150° before each experiment. Temperatures were measured with a chromel-alumel thermocouple calibrated at the tin and zinc points. The e.m.f. of this thermocouple was measured using the K-3 immediately before and after each measurement of cell potential, and the thermocouple e.m.f. at the time of measurement of the cell potential was interpolated from these data. The calculation of each temperature from the thermocouple-calibration data was made by an IBM 7094 computer as part of the general data analysis program.

Solvent. The solvent used was specially purified LiCl-KCl eutectic mixture obtained from Anderson Physics Laboratories, Inc., Champaign, Ill.; the method of purification used has been described previously.²⁰ Before use, each melt was tested for purity voltammetrically as described by Laitinen and Gaur.²¹

Chemicals. Platinum, iridium, and rhodium were supplied in wire form. Surface impurities were removed by successive treatments with HNO₃, HCl, and H₂O, after which the wires were dried at 150°. Graphite rods of 1/8-in. diameter, used as counterelectrodes in coulometric generation, were Grade U-1 Ultra Purity spectroscopic graphite electrodes (United Carbon Products, Inc., Bay City, Mich.) and were dried at 150° before use. Hydrogen and argon, delivered through two-stage regulators, were rendered oxygen-free and dried by passage over hot Cu and anhydrous Mg(ClO₄)₂. Hydrogen chloride, delivered through a two-stage regulator (Matheson 15RA-330), was purified by passage through activated charcoal and anhydrous Mg(ClO₄)₂. Mixtures of hydrogen and hydrogen chloride were prepared by mixing streams of the two purified gases in a 1.0-l. mixing chamber. Additional mixing and final removal of water vapor was done in a 1-ft. column packed with anhydrous Mg-

(ClO₄)₂ at the exit of the mixing chamber. The relative proportions of the two gases in the mixture could be roughly adjusted by use of flowmeters and needle valves (Series 620, Matheson Co., Joliet, Ill.).

Procedure

Rhodium and Iridium. A wire, cleaned as stated above, was immersed in an isolation compartment filled with eutectic in the cell. The system was allowed to equilibrate at 450° for 30 min. A platinum reference electrode of the type employed by Laitinen and Liu³ was generated in a separate isolation compartment. The rhodium or iridium wire was anodized using the coulometric current source and a graphite-rod counterelectrode in a separate isolation compartment. The anodization was interrupted from time to time, and, after waiting at least 10 min. to allow the solution to become homogeneous, the potential of the wire with respect to the platinum reference electrode was measured. The value of *n*, the electrochemical equivalents/mole of metal, was calculated from the weight loss of the wire. The concentration of the ionic species was calculated from argentometric determination of the chloride content of the isolation compartment.

Hydrogen(I)-Hydrogen. The central, narrow platinum flag of the hydrogen electrode, 3 by 0.2 cm., was flamed, cleaned as described above, platinized according to the procedure of Hills and Ives,²² rinsed, and dried at 150°. The hydrogen electrode was then assembled, flushed with purified argon, and inserted into the crucible containing molten eutectic to a depth of approximately 2 cm. The argon outlets of the hydrogen electrode and outer cell envelope were connected to sulfuric acid bubblers,⁴ which were adjusted to eliminate pressure differences between the separate atmospheres. These bubblers also served to prevent the contamination of the atmospheres within the hydrogen electrode and outer envelope by the external air or one another. With the temperature set at 450°, the melt penetrated the glass frit at the bottom of the hydrogen electrode, and the melt levels within the crucible and electrode became equal within 1-2 hr. This level was such that the inner gas delivery tube of the hydrogen electrode penetrated just below the level of the melt.

The argon atmosphere within the electrode assembly was then replaced by a mixture of hydrogen and hydrogen chloride taken from the mixing chamber described above. After about 1 hr., a stable (± 15 mv.) potential could be observed between the hydrogen electrode and a platinum reference electrode. A 1.5-l. reservoir was then filled with the gas mixture by displacement of mercury, a flow through the electrode being maintained during this filling process.

The hydrogen electrode was then isolated from the mixing chamber, and gas was supplied from the reservoir at a rate of approximately 0.8 cm.³/min. Variation of the flow rate by a factor of 3 in either direction had no effect upon the potential observed, which now had a variation of only ± 2 mv. The potential was measured with the temperature controller of the furnace set at 400, 450, and 500°. At least five values of the potential were recorded for each setting.

(20) H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).

(21) H. A. Laitinen and H. C. Gaur, *ibid.*, **104**, 730 (1957).

(22) G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 305 (1951).

Table I. Hydrogen Electrode Potentials

HCl gas press., mm.	Atmospheric press., mm.	Log <i>M</i> Pt(II) in reference	<i>E</i> _{cor.} , v.	Std. error	<i>dE/dT</i> , mv./deg. (cor.)	Std. error
541	733	-1.381	-0.68566	0.00018	-0.5434	0.0044
182	745	-1.152	-0.77449	0.00077	-0.6249	0.0127
25.7	745	-1.152	-0.99303	0.00029	-0.8345	0.0045
84.6	741	-1.334	-0.82984	0.00016	-0.7421	0.0032
299	741	-1.334	-0.73883	0.00010	-0.6002	0.0027
15.8	741	-1.334	-0.90152	0.00017	-0.8097	0.0038
44.5	735	-1.334	-0.85347	0.00017	-0.7596	0.0039
183	742	-1.334	-0.76566	0.00007	-0.6352	0.0016
473	742	-1.334	-0.68882	0.00031	-0.5265	0.0083
112	744	-1.334	-0.79981	0.00118	"	"
346	747	-1.382	-0.72808	0.00018	-0.5924	0.0045
625	745	-1.382	-0.64624	0.00043	-0.5108	0.0112
441	741	-1.331	-0.69639	0.00016	-0.5370	0.0040
663	741	-1.331	-0.62136	0.00012	-0.4507	0.0033
377	740	-1.331	-0.71010	0.00034	-0.5517	0.0083

^a Values taken only at 450°.

After completion of the potential measurements, the remaining gas in the reservoir was analyzed manometrically for hydrogen chloride by absorption on moist potassium hydroxide over mercury. Duplicate or triplicate analyses were run on 80-90-ml. samples of reservoir gas. The precision of these analyses was 1-2%. In certain cases the analyses were confirmed by argentometric titration of the resulting potassium chloride. The partial pressure of hydrogen chloride was calculated from these data, and that for hydrogen by difference, the total or atmospheric pressure being known. Correction of the atmospheric pressure for the effect of the sulfuric acid head was unnecessary as this head amounted to only 2-3 mm. of acid.

Results and Discussion

Rhodium(III)-Rhodium(0) and Iridium(III)-Iridium(0) Electrodes. A total of 96 potential-concentration data points were determined in four separate experiments using a rhodium wire as described above; the

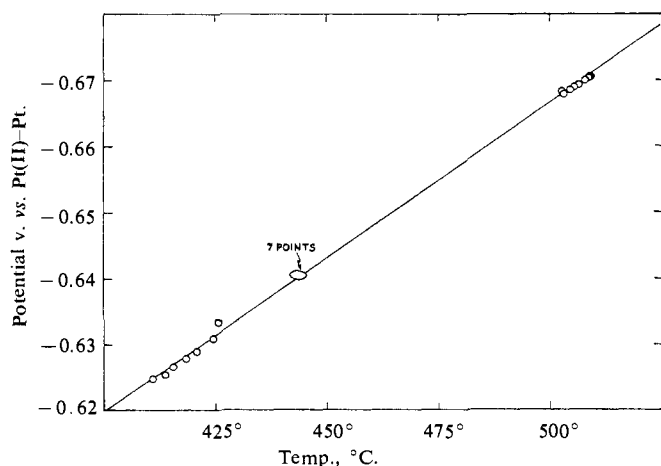


Figure 1. Temperature-potential graph for fifth data point in Table I. *P*_{HCl} = 299 mm., *P*_{H₂} = 442 mm.

range of concentrations studied was 0.2 to 0.002 *M*. The color of the rhodium solution was deep reddish brown. The coulometric value of *n* was 2.9 ± 0.3. The least-squares standard potential on the molarity

scale at 450° was -0.1959 (standard error 0.0039) v. vs. Pt(II) (1.0 *M*)-Pt. The experimental least-squares Nernst slope used in this calculation was 0.0438 (standard error 0.0023) as compared to the theoretical value of 0.0478.

A total of 135 data points was determined in four separate experiments employing iridium; the range of concentrations studied was 0.2 to 0.006 *M*. The color of the iridium solution was deep purple, and the coulometric value of *n* was 3.2 ± 0.3. The least-squares standard potential on the molarity scale at 450° was -0.0573 (standard error 0.0020) v. vs. Pt(II) (1.0 *M*)-Pt. The experimental least-squares Nernst slope was 0.0473 (standard error 0.0014).

Hydrogen(I)-Hydrogen Electrode. Several attempts to construct a workable hydrogen electrode in this melt were made before the procedure described above was developed. No stable potential could be obtained by saturating the molten eutectic with hydrogen chloride gas and bubbling a stream of hydrogen over a platinum electrode immersed in the melt, as in the case of the aqueous hydrogen electrode, since the hydrogen swept the hydrogen chloride out of the melt. Attempts to saturate the melt with hydrogen and to bubble a stream of hydrogen chloride proved equally unsuccessful, apparently for the same reason. The use of unplatinized, flamed platinum flags in a procedure otherwise like that finally developed produced stable (±2-3 mv.) potentials; however, these were somewhat lower than those observed on platinized flags for the same ratio of *P*_{HCl}/(*P*_{H₂})^{1/2}.

Between 15 and 48 measurements of the potential of the hydrogen electrode using the procedure described above were made for each mixture of hydrogen and hydrogen chloride. In all cases, the potential was found to be a linear function of the temperature. A representative graph (Figure 1) gives the experimental points and least-squares line for the fifth point given in Table I. Similar graphs were constructed for each hydrogen-hydrogen chloride mixture; the slopes, intercepts (at 450°), and standard errors were determined by a least-squares computer program and are given in Table I. Corrections for the individual platinum reference electrodes have been applied, and the potentials and temperature dependences are given

Table II. Comparison of Thermodynamic Quantities at 723°K.

Quantity	Value, N.B.S.	Value, JANAF	Value, this study ^a	Std. error, this study
ΔG° , kcal./mole	-23.623	-23.549	-23.433	0.115
ΔH° , kcal./mole	-22.383	-22.291	-22.316	0.133
ΔS° , cal./deg. mole	+1.714	+1.642	+1.614	0.254

^a One thermochemical calorie = 4.1840 joules.

with respect to the Pt(II) (1.0 M)-Pt standard reference electrode as defined previously.¹

These potentials and their temperature dependences were found to be linear functions of the logarithm of the pressure term $P_{\text{HCl}}/(P_{\text{H}_2})^{1/2}$; the slopes, intercepts, and standard errors were again calculated by a least-squares computer program. No significant increase in standard error was observed between data for one and for several runs, for either potential or temperature-dependence data.

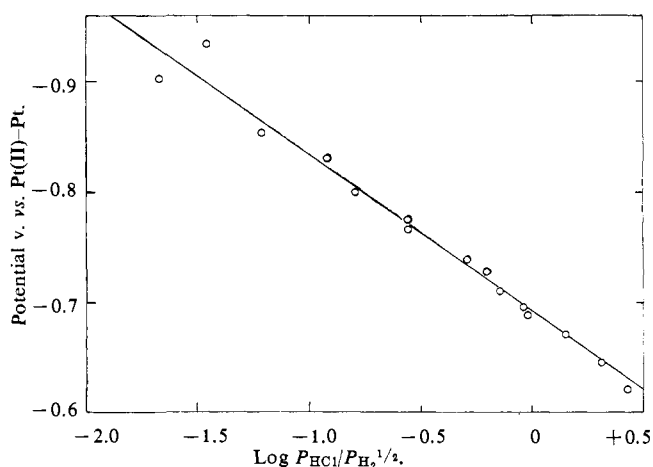


Figure 2. Variation of potential with $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$ (P in atm.).

A value of the standard potential of the half-reaction $1/2\text{Cl}_2 + e^- \rightarrow \text{Cl}^-$ in the LiCl-KCl eutectic at 450° has been reported⁴ as +0.3223 v. with a standard error of 0.0016 v. from a temperature-potential regression. A standard deviation for the three reference electrodes used was ± 0.0014 v., but this is probably primarily due to variation between the different types of reference electrodes used and, hence, should not be added to the standard error given. A very minor correction of +0.0003 v. should be used, however, to convert this value at 750 mm. to the standard state of 1 atm. Thus, the standard potential for the $\text{Cl}_2\text{-Cl}^-$ electrode is +0.3226 v.

For the half-reaction $\text{HCl} + e^- \rightarrow 1/2\text{H}_2 + \text{Cl}^-$, the standard potential determined in this study is -0.6935 ± 0.0047 v., where the error cited is the standard error of regression estimate from a potential vs. logarithm of pressure term regression (Figure 2). The slope is 0.1405 ± 0.0061 v./log unit as compared with the 0.1434 v./log unit expected for a one-electron reaction at this temperature. The data for the individual half-reactions can be combined so that, for the over-all reaction $1/2\text{H}_2 + 1/2\text{Cl}_2 \rightarrow \text{HCl}$ the standard potential is $+1.0161 \pm 0.0050$ v. since the standard error of a sum is the square root of the sum of the squares of the individual standard errors.²³

For an electrochemical reaction, $\Delta S = (\Delta E/\Delta T)_p$; this quantity was measured for the $\text{Cl}_2\text{-Cl}^-$ electrode as $-0.334 \pm 0.008 \times 10^{-3}$ v./deg. over the range 410-490°. In the case of the hydrogen chloride half-reaction, the temperature coefficient is not a constant but a linear function of the logarithm of the pressure term (Figure 3). The best straight line has a slope of $+0.1780 \pm 0.0097 \times 10^{-3}$ v./deg./log unit) and an intercept of $-0.5449 \pm 0.0075 \times 10^{-3}$ v./deg. at 450°. This temperature coefficient is given with reference to Pt(II) (1.0 M)-Pt. In order to combine data taken using platinum reference electrodes containing differing concentrations of platinum(II), the total e.m.f. of the cell $\text{H}_2, \text{HCl}, \text{Pt}|\text{LiCl-KCl}||\text{Pt(II)(C}_1)|\text{Pt}|\text{Pt(II)(C}_2)||\text{LiCl-KCl}|\text{Cl}_2, \text{C}$ must be considered in combining data for the hydrogen and chlorine work. A similar cell containing two hydrogen electrodes must be considered in combining data from different hydrogen electrode experiments. The temperature coefficient of such a cell employing two identical hydrogen electrodes will be $R/nF \ln(C_2/C_1)$; this factor was used to combine the temperature coefficient data. The values of ΔS° can be combined to give $+0.070 \pm 0.011 \times 10^{-3}$ v./deg. for the over-all reaction. The enthalpy of the over-all reaction can be calculated from the values given above using the well-known relationship $\Delta H = \Delta G + T\Delta S$.

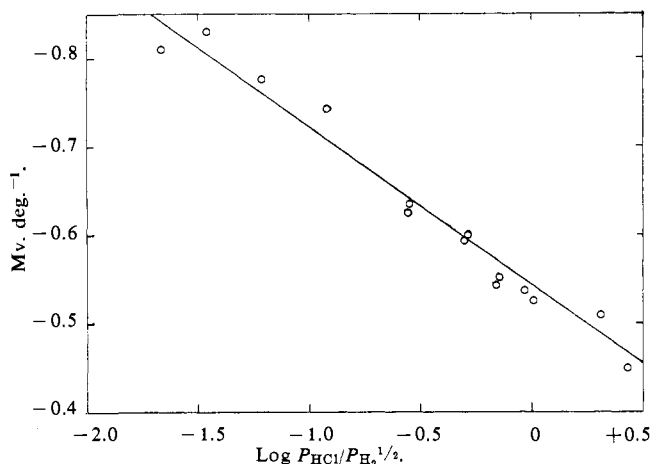


Figure 3. Variation of temperature coefficient with $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$.

The National Bureau of Standards has published²⁴ values of thermodynamic quantities for the reaction $1/2\text{H}_2(\text{g}) + 1/2\text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$ at 450°; the JANAF²⁵

(23) C. H. Goulden, "Methods of Statistical Analysis," John Wiley and Sons, New York, N. Y., 1939, p. 56.

(24) D. D. Wagman and W. H. Evans, "National Bureau of Standards (U. S.), Series III, Compilation," U. S. Government Printing Office, Washington, D. C., 1947-1956, Table 10-3.

(25) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1962.

tables are a more recent compilation. A comparison between the data of these tables and the values obtained in this study is given in Table II.

The agreement between the values given in the JANAF tables and those determined in this study is well within the experimental error of these measurements. Although the value of the free energy given in the N.B.S. tables differs from that determined in this study by more than the standard error of these measurements, this discrepancy is not considered significant. The magnitudes of the standard errors of the thermodynamic quantities calculated in this study are the same as those given in the JANAF tables for enthalpies and free energies calculated from aqueous electrochemical cell data and corrected to 25°; the standard errors obtained in this study are, however, considerably greater than those obtained in the extremely precise calorimetric measurements of Rossini²⁶ on the same reaction at 25°: $\Delta H^\circ_{\text{measd}} = -22.063 \pm 0.012$ kcal./mole and $\Delta G^\circ_{\text{calcd}} = -22.738 \pm 0.033$ kcal./mole.

(26) F. D. Rossini, *J. Res. Natl. Bur. Std.*, **9**, 679 (1932).

Table III. Standard Potentials at 450°

Electrode system	E°_M , v.	E°_m , v.	E°_X , v.
Pt(II)-Pt	0.000	0.000	0.000
Ir(III)-Ir	-0.057	-0.062	-0.092
Rh(III)-Rh	-0.196	-0.201	-0.231
HCl(g)-H ₂ (g), Pt	-0.694	-0.710	-0.800

The combination of the half-reactions used to calculate these values requires that the standard state of Cl⁻ ion be defined as that which prevails in the pure molten electrolyte. For a more detailed discussion, the reader is referred to the thesis of the junior author.¹

Standard potentials E°_M , E°_m , and E°_X , extrapolated to unit concentration on the molarity, molality, and mole fraction scales, calculated³ from the data of this study, are given in Table III. The correction term is applied only to the reference electrode in the case of the hydrogen chloride-hydrogen data.

The Influence of Ionic Strength on Polarographic Half-Wave Potentials. III. Theoretical Considerations of Systems Involving Complex Ions and the Investigation of the Cadmium Nitrate-Lithium Chloride Lithium Nitrate System¹

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Contribution from the Parkinson Laboratory of Southern Illinois University, Carbondale, Illinois. Received May 23, 1964

Previous investigations have shown the importance of including the effect of ionic strength of the system in considering the polarographic reduction of inorganic substances. This investigation is an attempt to correlate the effect of ionic strength on the equilibria involved in and on the interpretation of the polarographic data obtained from complex ion systems. In order to test these concepts, the half-wave potential of cadmium ion was determined in lithium nitrate-lithium chloride mixtures over the concentration range of 0-8 m including the various constant ionic strength systems. Application of theory indicates that above ligand concentrations of 1 m, a single complex system is present with an average number of bound ligands of 3.0 ± 0.1 and an over-all formation constant of 32 ± 5 .

Introduction

The importance of ionic strength in the polarographic reduction of inorganic and complex species in solutions of high concentrations of inert (supporting) electrolyte

(1) Taken from the Ph.D. Thesis of N. E. V., Southern Illinois University, June 1964.

(2) Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio.

has been illustrated.³⁻⁷ This work is an attempt to account for the effect of ionic strength in the polarographic investigation of complex ion systems, especially at electrolyte concentrations greater than 1 m.

Although the effect of ionic strength (usually constant) on the polarographic analysis of organic species has been known for some time,⁸ similar importance has not been emphasized in the investigation of inorganic systems, even though it has been implied (rather strongly⁷) on occasion. This communication will illustrate why such determinations should be carried out in systems of constant ionic strength, where at all possible. Although they are to be pointed out in greater detail subsequently, three of the problems which arise in the investigation of systems of high ionic strength they may become negligible at constant μ are

(3) D. E. Sellers and N. E. Vanderborgh, *J. Am. Chem. Soc.*, **86**, 1934 (1964).

(4) N. E. Vanderborgh and D. E. Sellers, *ibid.*, **86**, 2790 (1964).

(5) D. D. DeFord and D. L. Anderson, *ibid.*, **72**, 3918 (1950).

(6) H. M. Hershenson, M. E. Smith, and D. N. Hume, *ibid.*, **75**, 507 (1953).

(7) H. Irving, "Advances in Polarography," Vol. I, I. S. Longmuir, Ed., Pergamon Press, New York, N. Y., 1960, pp. 42-67.

(8) P. J. Elving, J. C. Komyathy, R. E. Van Atta, C. S. Tang, and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).