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### An Electromotive Force Series in Molten Lithium Chloride-Potassium Chloride Eutectic<sup>1</sup>

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Electrode potentials were measured in a lithium chloride-potassium chloride melt at 450° for a number of oxidation-reduction systems. The platinum(II)-platinum(0) system was used as a practical reference electrode which could be conveniently prepared by anodic dissolution of platinum with coulometric measurement of the amount dissolved. Most of the systems studied consisted of metal ion-metal couples with the metal ion in its lowest oxidation state. Other systems included Cr(III)-Cr(II) and Cu(II)-Cu(I). In general, the Nernst equation without an activity coefficient term was found to be applicable in dilute solutions.

Molten systems are of increasing importance as reaction media in a variety of technological applications, notably the manufacture of glasses and the electrowinning and electrorefining of metals. One of the main needs is an accurate evaluation of the oxidation-reduction potentials of various electrode systems. Such an evaluation is the objective of the present study.

A number of attempts have been made in the past to measure the decomposition potentials of different melts, the deposition potentials of various dissolved metal ions and the electromotive forces of concentration cells. Numerous types of reference electrodes have been developed for these measurements. A summary of these research reports is given elsewhere.<sup>2</sup>

However, few efforts have been spent in the systematic establishment of the electromotive forces of various metal ion-metal electrode systems in molten salts. Using the nickel system to provide the reference potential, Grjothheim measured the potentials of a number of metallic electrode systems in a sodium fluoride-potassium fluoride eutectic melt.<sup>3</sup> For measuring potentials in fused sodium chloride-aluminum chloride, Plotnikov, *et al.*, used an aluminum reference electrode which was separated from the solutions by a glass mem-

brane.<sup>4</sup> Chlorine on graphite was employed as the reference electrode by Rempel and Ozeryanaya in their studies on the electromotive forces of some heavy metals and their sulfides in molten alkali chlorides.<sup>5</sup> Skobets and Kavetski measured the potentials of metals containing 10 mole % of their bromides in alkali bromide-aluminum bromide baths, sodium or sodium amalgam sealed in a glass bulb serving as the reference electrode.<sup>6</sup> Delimarski and his co-workers made determinations on separate electrode potentials in chloride and bromide melts.<sup>7-9</sup> Delimarski also presented review articles on the electrode potentials in molten salts.<sup>10-11</sup> Stern and Carlton<sup>12</sup> measured electrode potentials in fused sodium hydroxide; potential-time curves were given.

#### Materials and Equipment

**Solvent.**—The eutectic mixture of lithium chloride-potassium chloride (melting point, 352°) was used at 450°.

(4) V. A. Plotnikov and E. I. Kirichenko, *Fortunatov, N. S., Zapiski Inst. Khim. Akad. Nauk, U.S.S.R.*, **7**, 159 (1940).

(5) S. I. Rempel and D. N. Ozeryanaya, *Zhur. Fiz. Khim.*, **25**, 1, 181 (1951).

(6) E. M. Skobets and N. S. Kavetski, *Zhur. Obshchei Khim.*, **10**, 1858 (1940).

(7) Y. K. Delimarski, L. S. Berenblum and I. N. Sheiko, *Zhur. Fiz. Khim.*, **25**, 398 (1951).

(8) Y. K. Delimarski and R. S. Khaimovich, *Ukrain. Khim. Zhur.*, **15**, 340 (1949).

(9) Y. K. Delimarski and A. A. Koloti, *Zhur. Fiz. Khim.*, **23**, 339 (1949).

(10) Y. K. Delimarski, *Ukrain. Khim. Zhur.*, **16**, 414 (1950).

(11) Y. K. Delimarski, *Zhur. Fiz. Khim.*, **29**, 28 (1955).

(12) K. H. Stern and J. K. Carlton, *J. Phys. Chem.*, **58**, 965 (1954).

(1) Sponsored by Office of Ordnance Research, U. S. Army. Abstracted from the Ph.D. thesis of C. H. Liu, 1957. Presented at the ACS meeting in Miami, Florida, April 9, 1957.

(2) C. H. Liu, Ph.D. thesis, University of Illinois, 1957.

(3) K. Grjothheim, *Z. physik. Chem.*, **11**, 150 (1957).

Preparation of the solvent was according to a procedure previously described.<sup>13,14</sup>

**Electrolytic Cell.**—The cell used in the experiments has been described previously.<sup>14,15</sup> Within the cell and under an argon atmosphere, the solvent was compartmented into separate portions by small tubes with fritted glass bottoms which acted as salt bridges.

**Furnace.**—Cenco-Cooley No. 13627, 115-volt, 700-watt (Central Scientific Co., Chicago, Illinois). A separate heating circuit which constituted 20% of the total heating capacity and which was regulated by the temperature controller was installed in the bottom of the furnace.

**Temperature Controller.**—Wheelco indicating controller Model 241-P (Barber-Coleman Co., Rockford, Illinois).

**Polarograph.**—Sargent Polarograph Model XXI (E. H. Sargent and Company, Chicago, Illinois). Period of rotation of voltage divider is 13.5 minutes, and maximum voltage span is 3 volts.

**Potentiometer.**—Student Potentiometer (Leeds and Northrup Co., Philadelphia, Pennsylvania).

**Constant Current Source.**—The source consisted of four 45-volt batteries in series and a cascade of fixed and variable resistors through which currents were drawn. The exact magnitude of the current was monitored by the potential drop across a standard resistor (Type 500, General Radio Co., Cambridge, Massachusetts) in the circuit, and changes in cell resistance and back e.m.f. were compensated by manually adjusting the variable resistors.

**Chemicals.**—The anhydrous metal chlorides were prepared as follows.

**Cadmium chloride and cupric chloride:** vacuum desiccation of analytical grade dihydrates over magnesium perchlorate.

**Bismuth chloride, lead chloride and thallos chloride:** commercially available anhydrous samples stored over magnesium perchlorate.

**Silver chloride:** precipitation from solutions of analytical grade sodium chloride and silver nitrate and subsequent desiccation over magnesium perchlorate.

**Zinc chloride, chromic chloride and aluminum chloride:** sublimation of commercially available anhydrous samples under a stream of dry hydrogen chloride. In the case of aluminum chloride, one sample was prepared by reaction of dry hydrogen chloride and aluminum at 200°.

**Manganese chloride:** desiccation of the tetrahydrate and dehydration of the resultant monohydrate at around 400° under a hydrogen chloride atmosphere.

**Indium trichloride:** direct combination of the elements.

**Stannous chloride:** reaction of dry hydrogen chloride with tin at 625°.

**Cuprous chloride,<sup>16</sup> gallium trichloride<sup>17</sup> and chromous chloride<sup>18</sup>:** procedures according to "Inorganic Syntheses"

### Definitions

**Nernst Equation.**<sup>19</sup>—It will be shown that the electrode systems studied in this work obey closely the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{red}}}$$

where

$E$  is the potential in volts  
 $E^0$  is the standard potential in volts  
 $n$  is the no. of electrons involved in electrode process  
 $C_{\text{ox}}$  is the concentration of the oxidant  
 $C_{\text{red}}$  is the concentration of the reductant  
 $R$ ,  $T$  and  $F$  have their usual thermodynamic significance

- (13) W. S. Ferguson, Ph.D. thesis, University of Illinois, 1956.  
 (14) H. A. Laitinen, W. S. Ferguson and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).  
 (15) H. A. Laitinen and W. S. Ferguson, *Anal. Chem.*, **29**, 4 (1957).  
 (16) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 1.  
 (17) H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 26.  
 (18) L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 150.  
 (19) The sign convention as recommended by the IUPAC in the *Compt. rend. of the XVllth Conference, Stockholm, 1953*, is used here.

At 450°, the equation becomes

$$E = E^0 + \frac{0.1434}{n} \log \frac{C_{\text{ox}}}{C_{\text{red}}}$$

As will be shown, for a metal ion in solution, the activity coefficient for the ion is either unity or a constant for the concentration range examined. Thus, unless the conditions are changed (for instance, by changes in composition or in operation temperatures), either the activity is identical with the concentration or the activity coefficient term can be incorporated as a constant in the  $E^0$  term.

**Standard States and Standard Potentials.**—To express concentration, three scales can conveniently be used. These are molarity, molality and mole fraction. If the assumptions are made that the quantity of the solute is negligible compared to that of the solvent and that the density of the solution is the same as that of the solvent, it can be shown that

$$M = \frac{W_s d}{M_s N M_0} \times 10^3$$

$$m = \frac{W_s}{M_s N M_0} \times 10^3$$

$$X = \frac{W_s}{M_s N}$$

where

$M$  is the molarity  
 $m$  is the molality  
 $X$  is the mole fraction  
 $W_s$  is the weight of the solute in g.  
 $M_s$  is the formula weight of the solute  
 $M_0$  is the av. formula weight of the solvent  
 $N$  is the no. of moles of chloride in soln.  
 $d$  is the density of the solvent in g./ml.

At 450°, the density of the eutectic melt is 1.648 g./ml.<sup>20</sup> and the conversion factors are

$$X = 0.0337M$$

and

$$m = 0.607M$$

The advantage of molality and mole fraction over molarity is that the former two do not involve the density of the melt and are independent of temperature.

The standard state for a metal ion is unit concentration except for  $\text{Li}^+$ , for which the prevailing activity in the eutectic mixture was adopted as the standard state. For pure metals, the standard state is defined as its physical state at 450° under one atmosphere pressure and taken as unity. The standard potential of an electrode system is its potential at unit ratio of oxidant to reductant activity. Thus, for the three concentration scales, there are three standard potentials for each electrode system. These are designated as  $E^0_M$ ,  $E^0_m$ , and  $E^0_X$  for the molarity, molality and mole fraction scales, respectively.

**Reference Standard Potential.**—Since the platinum(II)–platinum(0) system has been employed as the reference electrode in the potential measurements, its standard potential is arbitrarily and conveniently assigned the value 0.000 volt and used as the reference point in the electromotive force series. The standard potentials of other electrode systems will then be relative to this value.

- (20) E. R. Van Artsdalen and I. S. Yaffe, *J. Phys. Chem.*, **59**, 118 (1955).

TABLE I<sup>a</sup>  
 STANDARD POTENTIAL MEASUREMENT ON THE NICKEL(II)-NICKEL(0) SYSTEM

Equiv. of electricity passed $\times 10^4$	Moles generated $\times 10^4$	Molarity, $M$	Log $M$	$E$ , v., measured	$E$ , v. vs. 1 $M$ Pt reference	$E^{\circ}_M$
2.464	1.232	$3.394 \times 10^{-2}$	-1.469	-0.8016	-0.8991	-0.7937
4.970	2.485	$6.846 \times 10^{-2}$	-1.165	- .7814	- .8789	- .7954
7.460	3.730	$1.028 \times 10^{-1}$	-0.988	- .7676	- .8651	- .7942
9.950	4.975	$1.370 \times 10^{-1}$	-0.863	- .7590	- .8565	- .7946

<sup>a</sup> The volume of the melt present was 3.63 ml. The platinum(II) concentration in the reference electrode was  $4.370 \times 10^{-2} M$ .

The chlorine-chloride electrode perhaps should be regarded as the ultimate reference for electrode potentials in chloride melts. However, it has the practical disadvantages of being less convenient than the platinum reference. Moreover, the temperature coefficient of the e.m.f. of cells made up of two metal-metal ion electrodes is generally much smaller than that of a metal-metal ion electrode measured against the chlorine electrode.

Other reference systems which have been examined are the silver chloride-silver and the lithium (I)-lithium electrodes.<sup>21</sup>

### Experimental Procedures

The procedures for evaluating the standard potential on the molarity scale will now be described. Conversion to the other concentration scales will be discussed in a later section.

**Reference Electrode.**—For each experiment, a fresh reference electrode was constructed by anodizing at a constant current for a known period of time a platinum foil in a compartment of melt to generate platinum(II) coulometrically. The current density was usually  $5 \times 10^{-3}$  to  $1 \times 10^{-2}$  ampere per square centimeter. From the number of electrolytic equivalents passed and the chloride content of the compartment, as determined by titration with silver nitrate, the exact concentration of platinum(II) in the reference electrode compartment was calculated. The range of the concentration was 0.01 to 0.1 molar. The potentials measured for the other electrode systems were then extrapolated by the use of the Nernst equation to values *versus* a one molar platinum(II)-platinum(0) potential, arbitrarily taken as 0.000 volt. The applicability of this equation was checked by potential measurements upon concentration cells of platinum(II) solutions. A reference electrode was first constructed, and another platinum foil was anodized at a constant current for successive intervals of time. The potential after each period of anodization was measured against the reference electrode and corrected to a value *vs.* the reference standard potential, that is, one molar platinum(II). The concentration of platinum(II) associated with each potential measurement and corresponding to a different period of electrolysis was calculated after the usual chloride determinations. A plot of the logarithm of concentration *versus* potential is given as Curve 3, Fig. 1, the line is theoretical and based upon the standard potential of 0.000 volt, and the circles are experimental points. For each potential measured, an experimental standard potential was calculated by the use of the Nernst equation. While the theoretical value is 0.000 volt, the experimental result which was an average of all the measurements was -0.001 volt with an average deviation of  $\pm 0.001$  volt. This slight disagreement is considered within the experimental error.

**Potential Measurements.**—The electrode systems studied can in general be divided into four categories, and the experimental approaches differ for each.

The first group consists of metals whose melting points are higher than the operating temperature, which are available in foil or rod form or are easily machinable, and whose chlorides are not volatile from the melt. Included in this group of electrode systems are: gold(I)-gold(0), palladium(II)-palladium(0), antimony(III)-antimony(0), silver(I)-

silver(0), nickel(II)-nickel(0), copper(I)-copper(0), cobalt(II)-cobalt(0), iron(II)-iron(0), chromium(II)-chromium(0), manganese(II)-manganese(0) and magnesium(II)-magnesium(0). Antimony(III) chloride is quite volatile at higher concentrations, but volatilization is slow at a low concentration. The usual procedure was to anodize at a constant current the metal in question in a fritted compartment. The current density ranged from  $5 \times 10^{-3}$  to  $1 \times 10^{-2}$  ampere per square centimeter. Solutions of the ions of the metal in its lowest oxidation state were produced. The potentials at this electrode after successive periods of electrolysis and thus at various concentrations of the metal ion were measured against the reference electrode. Again, the exact concentrations were calculated from the number of coulombs passed and the volume of the melt present which was determined by argentometric titrations after the experiment. The "*n*" value of the electrolytic oxidation, that is, the number of equivalents per mole of the metal ion, was checked by measuring the number of faradays of electricity passed and by determining the weight loss of the wire or the total amount of metal ions in solution with appropriate analytical methods. In all cases, results indicated a current efficiency of close to 100% for the anodic processes within the current density range employed. The chief assumption in this procedure is that contribution to the transport process by the metal ions produced is very small or, in other words, that the amount of metal ions moving out of the anode compartment toward the cathode during the electrolysis is negligible. In view of the high concentration of chloride, lithium ion and potassium ion, this assumption is fully justified. The concentration range of the metal ions studied was usually 0.001 to 0.5 molar. The potentials measured at various concentrations were extrapolated by the use of the Nernst equation to standard potential values. Table I gives a set of representative data on the nickel(II)-nickel(0) system.

An alternate procedure is to dissolve successively weighed amounts of an anhydrous metal chloride into the melt and measure the potential after each addition, a foil or rod of the pure metal serving as the indicator electrode.

Metals which are liquids at the operating temperature and whose chlorides are not volatile from the melt constitute the second group of electrode systems, which includes tin(II)-tin(0), lead(II)-lead(0), cadmium(II)-cadmium(0), thallium(I)-thallium(0) and zinc(II)-zinc(0). Since anodization of liquid metal pools was unsuccessful due to practical difficulties in the cell design, solutions of the metal ions were prepared by the addition of the anhydrous chlorides to the melt. The liquid metal was deposited cathodically at a constant current onto an inert base metal rod, usually tungsten, which served as the indicator electrode. The concentration of the metal ions was diminished after successive intervals of cathodization, and the potential of the system was measured after each interval. The exact concentration at each potential measurement was calculated from the amount of solute put in, the moles consumed by electrolysis, and the volume of the melt present. The standard potential was then calculated as before. Precautions were taken not to use an excessive current density during the electrolysis, for if the concentration of the metal ion in question was insufficient to maintain the current, lithium would be deposited to introduce mixed potentials and make accurate potential determinations completely impossible. The current density ranged from  $1 \times 10^{-3}$  to  $5 \times 10^{-3}$  ampere per square centimeter. The "*n*" values were obtained by examining the polarographic reduction waves. Alternately, techniques applicable to the third category of metals also have been used here.

The third group of electrode systems, which includes bis-

(21) (a) H. A. Laitinen and C. H. Liu, unpublished work, monthly reports, Contract No. DAL-49-186-502-ORD(P)-187, University of Illinois; (b) unpublished work, status reports, Contract No. DAL-11-022-ORD-1987, University of Illinois.

muth(III)-bismuth(0), indium(III)-indium(0), gallium(III)-gallium(0) and aluminum(III)-aluminum(0), are composed of metals whose chlorides are volatile from the melt to different extents. For the aluminum(III)-aluminum(0) system, a small quantity of the anhydrous chloride was added to the melt. An aluminum wire or foil was immediately introduced into the solution, and the potential was measured. The concentration of aluminum(III) was evaluated as before. By this method, only very low concentrations were obtainable; for if the concentration was too high, the rate of volatilization was sufficiently rapid to introduce significant errors. To secure the potential at higher concentrations and to determine a coulometric "n" value, a different approach was required. A weighed aluminum wire (surface area two square centimeters) was immersed in the melt and anodized at twenty milliamperes for two hours; at the end of this period of electrolysis, the system was allowed to stand ten minutes to permit the attainment of equilibrium. Immediately after the potential was read, the compartment containing the aluminum(III) solution was removed from the bulk of the melt, and the contents were poured out and cooled quickly. The total aluminum(III) present was then determined gravimetrically with 8-quinolinol. The concentration of aluminum(III) in the melt at the time of potential measurement was then calculated after the argentometric determination of the chloride content of the compartment. From the weight loss of the wire, the "n" value was 2.81 as determined coulometrically. For the other systems in this group, the metals are liquid at the operating temperature. The chlorides are far less volatile from the melt than aluminum chloride as shown by successive polarograms and analyses of the solutions after standing. Their volatilization from the melt for a short period of time was considered negligible. In these cases, after a weighed addition of the anhydrous chloride, a microelectrode (tungsten except in the case of the bismuth system where platinum was used) was immediately immersed in the solution and a small amount of the metal deposited. This plated microelectrode then served as the indicator electrode for the measurement of potentials. The time required to deposit the metal and to measure the potential was usually less than ten minutes. The standard potentials were then evaluated in the usual manner.

The fourth group includes the copper(II)-copper(I) and chromium(III)-chromium(II) systems where both the oxidized and the reduced species are soluble in the melt. There were indications that these electrode systems might not be sufficiently reversible to give good potentiometer readings. The procedure used in evaluating the copper(II)-copper(I) standard potential will now be described. A graphite rod one-sixteenth inch in diameter which had been cleaned and dried and which was connected to the outside with platinum wire was lowered into a melt compartment. A residual current curve of the melt was run on the Sargent Polarograph Model XXI with the rod as the indicator electrode against a platinum reference electrode. A known amount of copper(I) was then put into solution by the anodization of a copper foil, and a weighed portion of cupric chloride was added to form a mixture of known concentration ratio. Potentials were again applied between the reference electrode and the rod which had been immersed in the solution. When the potential was reached where the net electrolytic current changed sign (or, in other words, the total current reached a value equal to the residual current), the leads from the polarograph were disconnected from the electrodes, and the potential between these leads was measured with the potentiometer. In this manner, inherent potential reading errors on the polarograph were eliminated, and a more accurate potential reading was obtained. This potential represented the equilibrium value at that particular concentration ratio. Successive portions of cupric chloride were then added, and the same procedure was repeated after each addition to obtain potentials at various concentration ratios. The standard potential was then evaluated by the use of the Nernst equation to extrapolate to unit concentration ratio. The concentration of copper(I) was  $1$  to  $2 \times 10^{-1} M$ . Similar techniques were applied in the case of the chromium(III)-chromium(II) system except a platinum microelectrode instead of a graphite rod was used as the indicator electrode. Chromium(II) was coulometrically generated from chromium metal, and chromium(III) was added as weighed portions of chromic chloride. Solutions of known concentration ratios were also prepared by

cathodization of chromium(III) solutions and anodization of chromium(II) solutions with a platinum foil electrode.

The lithium(I)-lithium(0) system presented special problems. Molten lithium in the presence of the chloride melt is extremely reactive and attacks glass very rapidly. Attempts at depositing lithium onto graphite and tungsten rods were met with failure as no stable potential readings could be registered. Finally, the standard potential of this system was determined in the following manner. Pure lithium metal was cut into small strips under a dry argon atmosphere. Commercial zirconia tubes with closed bottoms, procured from the Norton Company, were leached with aqua regia, thoroughly washed with water, dried at elevated temperatures and put into the eutectic melt. They were quite permeable to the fused eutectic. The lithium strips were then dropped into these tubes to form liquid lithium pools which, because of the low density of lithium, floated on top of the melt. Molten lithium, with a higher surface tension than the melt, did not leak through the fine pores of the zirconia tubes in any appreciable amount. A clean tungsten wire was then used to make contact from the lithium pool to the outside while the potential of the pool in equilibrium with the lithium(I) of the melt was measured against a reference electrode with the potentiometer. In computing the standard potential, the solvent concentration of lithium(I), which is 17.39 molar, was used instead of unit concentration as a matter of convenience. Thus, the only extrapolation involved is that of correcting the reference electrode to unit concentration of platinum(II). The measured potential fluctuated slightly with time, and the average of a number of readings was taken as the final experimental value. Table II illustrates this fluctuation.

TABLE II<sup>a</sup>  
STANDARD POTENTIAL MEASUREMENT ON THE LITHIUM(I)-LITHIUM(0) SYSTEM

Time, min., after introducing lithium	$E$ , v., measured	$E_M^0$
20	-3.2090	-3.3065
60	-3.2070	-3.3045
120	-3.2046	-3.3021
150	-3.2038	-3.3013
180	-3.2024	-3.2999
210	-3.2070	-3.3045
360	-3.2048	-3.3023

<sup>a</sup> The platinum(II) concentration in the reference electrode was  $4.370 \times 10^{-2} M$ .

The mercury(II)-mercury(0) potential was roughly estimated from the polarogram of mercury(II). The concentration of mercury(II) was approximated by comparing the wave height with that of a cadmium(II) wave on the same microelectrode at a known cadmium(II) concentration. The assumption was that since both reductions involved two electrons, equal concentrations should give rise to reduction currents fairly close to each other in magnitude. The half-wave potential of the mercury(II) wave was taken as the equilibrium potential at the estimated concentration.

The chlorine-chloride standard potential has been carefully evaluated by Mr. J. W. Pankey of this Laboratory in his research work and is included here merely to show the potential span of the eutectic melt.<sup>22</sup>

## Results and Discussions

For each electrode system, a plot of the logarithm of molarity *versus* potential against one molar platinum reference electrode has been made. These plots are given in Figs. 1, 2, 3 and 4. The lines are theoretical, based upon the Nernst equation and the standard potential values established in this work; the circles represent experimental points.

The standard potentials computed for all three concentration scales are listed in Table III. To convert  $E_M^0$  to  $E_m^0$  and  $E_X^0$ , for the metal ion-metal systems involving two electrons, no change is nec-

(22) H. A. Laitinen and J. W. Pankey, unpublished work, status reports, contract No. DAI-11-022-ORD-1987, University of Illinois.

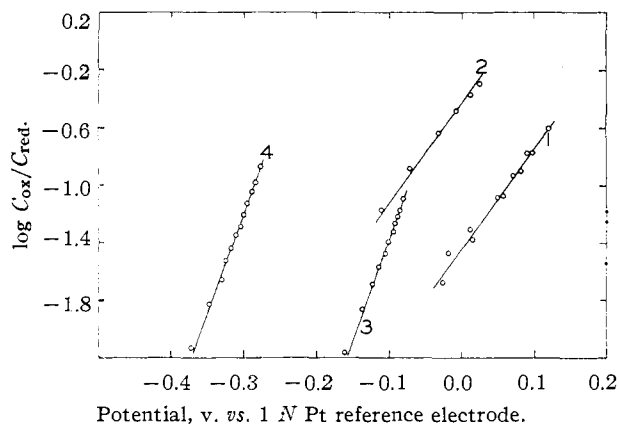


Fig. 1.—Nernst equation plots: 1, Au(I)-Au(0); 2, Cu(II)-Cu(I); 3, Pt(II)-Pt(0); 4, Pd(II)-Pd(0).

essary for the corrections for the reference electrode and for these systems cancel out. For the one electron system, the correction terms from  $E_M^0$  to  $E_m^0$  and  $E_X^0$  are 0.016 and 0.106 volt. For the three electron systems, these terms are -0.005 and -0.035 volt. In the case of the electrode systems copper(II)-copper(I), chromium(III)-chromium(II), lithium(I)-lithium(0) and chlorine-chloride, a correction on the reference electrode alone was involved.

TABLE III<sup>a</sup>  
ELECTROMOTIVE FORCE SERIES

Electrode system	$E_M^0$	$E_m^0$	$E_X^0$
Li(I)-Li(0)	-3.304	-3.320	-3.410
Mg(II)-Mg(0)	-2.580	-2.580	-2.580
Mn(II)-Mn(0)	-1.849	-1.849	-1.849
Al(III)-Al(0)	-1.762	-1.767	-1.797
Zn(II)-Zn(0)	-1.566	-1.566	-1.566
Tl(I)-Tl(0)	-1.476	-1.460	-1.370
Cr(II)-Cr(0)	-1.425	-1.425	-1.425
Cd(II)-Cd(0)	-1.316	-1.316	-1.316
Fe(II)-Fe(0)	-1.171	-1.171	-1.171
Pb(III)-Pb(0)	-1.101	-1.101	-1.101
Sn(II)-Sn(0)	-1.082	-1.082	-1.082
Co(II)-Co(0)	-0.991	-0.991	-0.991
Cu(I)-Cu(0)	-.957	-.941	-.851
Ga(III)-Ga(0)	-.84	-.84	-.88
In(III)-In(0)	-.800	-.805	-.835
Ni(II)-Ni(0)	-.795	-.795	-.795
Ag(I)-Ag(0)	-.743	-.727	-.637
Sb(III)-Sb(0)	-.635	-.640	-.670
Bi(III)-Bi(0)	-.553	-.558	-.588
Cr(III)-Cr(II)	-.525	-.541	-.631
Hg(II)-Hg(0)	-.5	-.5	-.5
Pd(II)-Pd(0)	-.214	-.214	-.214
Pt(II)-Pt(0)	.000	.000	.000
Cu(II)-Cu(I)	.061	.045	.045
Au(I)-Au(0)	.205	.221	.311
Cl <sub>2</sub> -Cl <sup>-</sup>	.322	.306	.216

<sup>a</sup> The standard potentials are given in volts.

The standard potential values, which are the average values of a number of measurements, usually have standard deviations of  $\pm 0.001$  to  $\pm 0.002$  volt. Exceptions are chromium(III)-chromium(II) with  $\pm 0.010$ , indium(III)-indium(0) and aluminum(III)-aluminum(0) with  $\pm 0.009$ , gold(I)-

gold(0) and manganese(II)-manganese(0) with  $\pm 0.008$ , copper(II)-copper(0) with  $\pm 0.004$ , and cobalt(II)-cobalt(0) and chromium(II)-chromium(0) with  $\pm 0.003$  volt.

In the case of the gallium(III)-gallium(0) system, the standard potential evaluated on the basis of a three electron process was  $-0.843 \pm 0.020$  volt. The experimental points, however, lie on a line with a slope of 0.132 which is close to a theoretical one electron slope of 0.1434. Since gallium trichloride was added to the melt, gallium(I), if it were in solution, would have to be the decomposition product of the gallium(III) chloride. There is evidence that this decomposition could not have occurred to any pronounced extent. First of all, there was no indication of the presence of chlorine which would have given rise to a cathodic current at all potentials on a polarogram run with a platinum or tungsten microelectrode. Secondly, when the solution of the gallium salt was taken out and dissolved in water, no hydrous oxide of gallium(III) was observed. Thirdly, the polarographic reduc-

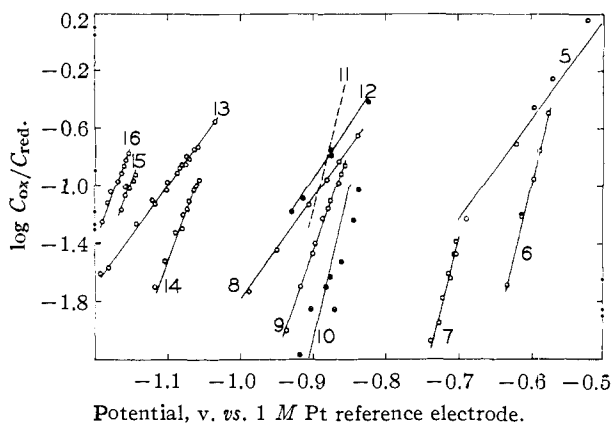


Fig. 2.—Nernst equation plots: 5, Cr(III)-Cr(II); 6, Bi(III)-Bi(0); 7, Sb(III)-Sb(0); 8, Ag(I)-Ag(0); 9, Ni(II)-Ni(0); 10, In(III)-In(0); 11, Ga(III)-Ga(0), theoretical; 12, Ga(III)-Ga(0), experimental; 13, Cu(I)-Cu(0); 14, Co(II)-Co(0); 15, Sn(II)-Sn(0); 16, Pb(II)-Pb(0).

tion currents of bismuth chloride and gallium trichloride were comparable for similar concentrations and electrode areas. At the same time, due to the extremely hygroscopic nature of gallium trichloride, serious difficulties were experienced in its weighed addition into the melt. Therefore, the scattering of the points probably is attributable to contamination by moisture. The resultant hydroxide or oxide ion could combine with the gallium(III) to form a complex species which would then introduce mixed potentials in the measurements. Undoubtedly, a better experimental procedure needs to be devised before more exact measurements can be made.

The reproducibility of these potentials from experiment to experiment has been taken as the criterion for judging their validity, and potential measurements on each system have been repeated in at least two or more experiments.

Three possible sources of error are evident. The first is the diffusion and leakage of metal ion solu-

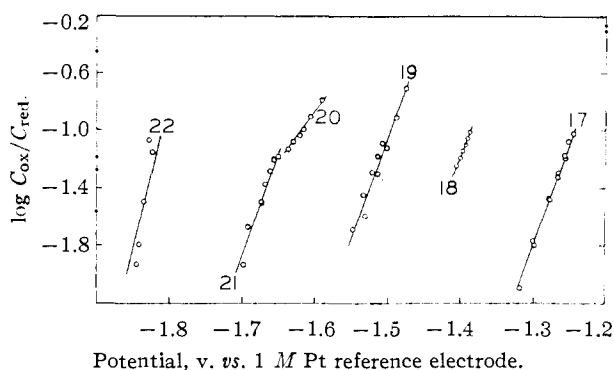


Fig. 3.—Nernst equation plots: 17, Fe(II)–Fe(0); 18, Cd(II)–Cd(0); 19, Cr(II)–Cr(0); 20, Tl(I)–Tl(0); 21, Zn(II)–Zn(0); 22, Al(III)–Al(0).

tions out of the fritted compartments and of bulk melt into them. However, when care is taken in performing the experiments, errors arising from this source are probably negligible. The second source of error is related to the fact that the melt always gives a residual current, especially at more negative potentials as shown by the residual current curves on microelectrodes. Except for the copper(II)–copper(0) and chromium(III)–chromium(II) systems, the measured potentials were all zero current potentiometer readings. Thus, a small but perhaps not negligible amount of anodic current had to be drawn to counter-balance the residual cathodic current. Thirdly, for some potential measurements, especially those involving liquid metals, a base metal or a foreign metal connection wire was used either in or close to the melt. Therefore, there might have been an appreciable though reproducible thermal junction potential. It was observed however that for the cadmium(II)–cadmium(0) system, the potential was not significantly different whether platinum or tungsten was used as the base metal.

### Conclusion

The electromotive force series established will aid in predicting the course of chemical reactions in the melt. Analytically, these standard potential values are not only directly applicable to quantitative determinations by the linear relationship between the logarithm of concentration and po-

tential but also extremely useful in providing the basis for other analytical procedures.

The application of the compiled electromotive force series to melts other than the lithium chloride–potassium chloride eutectic should be judicious; for the electrode systems may not be reversible in these melts, and the potential determining ionic species are likely to be different. Changes in potential values and reversal in order should not be uncommon. Thermodynamically, it would appear at the first glance that the standard potential on the mole fraction scale could be used to evaluate the formation potential, or the free energy of formation, of the chloride of the potential determining ionic species, be it simple or complex in form. In some recent work,<sup>23</sup> this method of evaluation has been discussed in detail. However, it should be kept in mind that the computation of these values involves extrapolations three orders in magnitude and that the pure compound in liquid form and its dilute solution in the eutectic melt represent in effect two entirely different solvent sys-

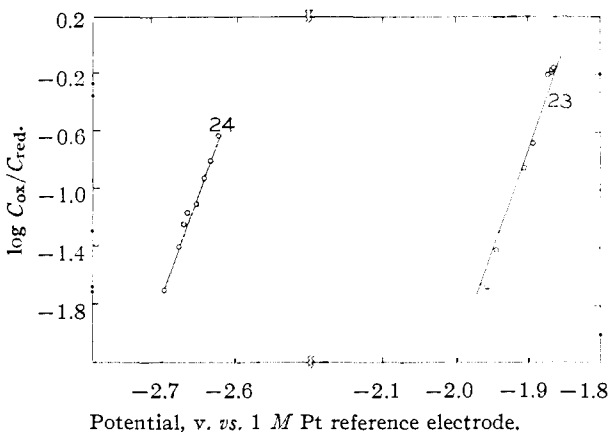


Fig. 4.—Nernst equation plots: 23, Mn(II)–Mn(0); 24, Mg(II)–Mg(0).

tems. Thus, these potential values should be used only for dilute solutions and perhaps only within the concentration range where measurements were made.

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(23) R. D. Walker and D. E. Danly, paper presented at the Oak Ridge Molten Salt Symposium, July, 1957.