

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

Polarography in Fused Salts¹BY MARTIN STEINBERG² AND NORMAN H. NACHTRIEB

The application of the polarographic method to the study of fused salt solutions has been attempted only recently. Lyalikov and Karmazin,³ employing a solid platinum microelectrode which was periodically dipped into the solutions by means of a gas bubbler system, obtained polarographic current-voltage curves for a number of ions dissolved in a potassium nitrate melt. In some cases they found a linear relation between wave height and concentration. A disadvantage in the use of such electrodes is that the diffusion field is inhomogeneous, and an exact mathematical analysis of the process has not been possible. Diffusion up to a growing spherical drop electrode of liquid metal has been worked out in detail,^{4,5} however. The use of such electrodes permits the calculation of a number of useful quantities, *viz.*, diffusion coefficients, activation energies for diffusion, and amalgam electrode potentials. In a study with a ternary eutectic melt of lithium nitrate, ammonium nitrate, and ammonium chloride the authors⁶ found that the Ilkovic equation is applicable to the reduction of nickelous ion at the dropping mercury electrode. This eutectic solvent was visibly unstable, and the investigation was continued with a low-melting ternary mixture of lithium, sodium and potassium nitrates. The results of the latter study and some attempts to operate dropping liquid metal electrodes other than mercury at higher temperatures are reported in the following. The ultimate objective, not yet attained, is the development of a polarographic technique for the study of reactions in metallurgical slags and molten glasses.

Experimental

The Solvent.—Melts were prepared to contain 30 mole % lithium nitrate, 17 mole % sodium nitrate, and 53 mole % potassium nitrate by heating the C. P. salts to 200° in an open beaker. Cooling curves obtained on portions of the melts showed the onset of crystallization at 145° and a long eutectic halt at 120°, in agreement with the phase diagram determined by Carveth⁷ for this system. To provide chloride ion for the use of a calomel reference electrode 0.5 mole of potassium chloride was added per 100

moles of the ternary salt mixture. A supporting electrolyte is unnecessary because of the highly ionic character of the solvent. The homogeneous melt was cooled to 150° and poured into evaporating dishes in order to solidify the salts rapidly and thereby maintain uniform composition.

The density of the melt, containing added potassium chloride, was determined from its buoyant effect on a lead-weighted Pyrex bob. The bob hung from one arm of an analytical balance and dipped into the melt, which was heated in a resistance-wound vertical tube furnace. The density of the melt over the range 160 to 260° is given by

$$d_s = 2.103 - 7.9 \times 10^{-4}t \quad (1)$$

where *t* is the centigrade temperature. This equation was used throughout for the purpose of referring solute concentrations to a molar basis.

Portions of the ternary salt containing added chloride and weighing from 30 to 40 g. were melted in beakers; weighed amounts of various solute salts were added to provide solutions of the desired concentrations. The melts were maintained at 160° while dry nitrogen was passed through them to remove water and to stir the solutions. When many experiments were to be done with the same solute a master solution was prepared at 160°, rapidly solidified, and stored over phosphorus pentoxide. Solutions of lower solute concentration were prepared by melting together weighed portions of the master salt and pure solvent salt.

Cells.—The cells employed in the study are shown in Fig. 1. Pyrex tubing was used for the vessels and jackets; capillaries⁸ and the tubes to which they were sealed were constructed of lead glass. The capillaries were of such lengths as to yield mercury drop times of 2 to 4 seconds under pressures of 40 to 60 cm.

Cell 1 was used to obtain most of the data. Electrolyses were conducted in the inner vessel between the drop and the anode pool, which were maintained at either fixed or variable potential differences by means of the slidewire of the polarograph. The a. c. resistance of the salt-filled cell was about 100 ohms, and caused a negligible *iR* drop of a few millivolts through the cell. All potential measurements on the drop were made with a student type potentiometer against an external calomel reference electrode in the bottom of the outer jacket. Contact between the two halves of the cell was established through a salt-filled annular bridge between a 5 mm. o. d. sleeve and a 3 mm. o. d. tube in which was sealed the platinum lead (A) to the reference electrode. Use of the bridge to separate the calomel from the drop improved the stability of the cell. A micro-funnel was arranged to swing under the capillary to collect the mercury drops for subsequent removal and weighing. To place cell 1 in operation it was preheated at 160° with about 10 mg. of mercurous chloride in the bottom of the outer jacket. This amount of calomel was far more than enough to saturate the solution in the reference electrode compartment. About 35 g. (18 cc.) of the molten salt solution was then poured into the inner vessel and allowed to flow through the sleeve. The cell was then assembled. Mercury was added to the inner and outer vessels to form the anode pool and reference electrode, respectively. Not shown in the drawing was a tube for bubbling dry nitrogen through the melt for thirty minutes prior to each run for the purpose of removing water and facilitating the attainment of thermal equilibrium. During the recording of a polarogram the bubbler tube was raised and the nitrogen allowed to flow over the melt.

(8) Obtained from the Corning Glass Works as "Marine Barometer Tubing."

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(3) Yu. S. Lyalikov and V. I. Karmazin, *Zapodskaya Lab.*, **14**, 144 (1948).

(4) D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **6**, 498 (1934).

(5) D. MacGillivray and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(6) N. H. Nachtrieb and M. Steinberg, *THIS JOURNAL*, **70**, 2613 (1948).

(7) H. R. Carveth, *J. Phys. Chem.*, **2**, 209 (1898).

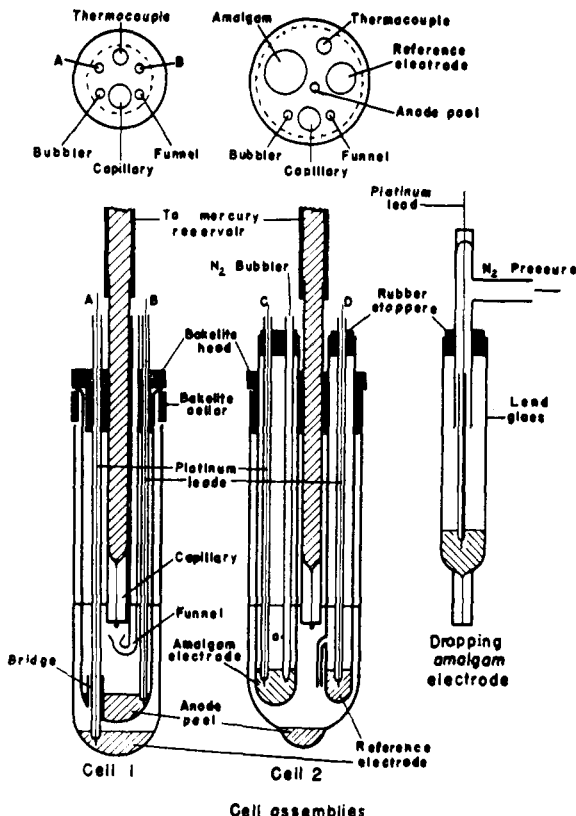


Fig. 1.

Cell 2 was used to obtain potentials of stationary amalgam electrodes against fused salt solutions of the ions of the amalgamated metals in addition to polarograms. The calomel reference electrode made contact with the solution through a bridge made of 3-mm. tubing. The stationary amalgam electrode was contained in a 12-mm. tube with a small hole in its side above the amalgam surface to contact the main body of the solution. Platinum leads sealed in Pyrex served to connect the amalgam pool, reference electrode, and anode pool to the external circuit. Nitrogen was bubbled through the amalgams to expose fresh surface to the solutions; by means of another bubbler (shown only in plan view) nitrogen was passed either over or through the cell electrolyte, as for cell 1.

Both types of cells were heated with vertical, nichrome-wound tube furnaces in which windows were cut to permit illumination and viewing of the drops. Temperatures were held to $\pm 1^\circ$ with manually-operated variable transformers. A Sargent Model XXI Polarograph was used throughout the work.

Data and Discussion

Qualitative Survey.—Polarograms run at 160° on the ternary nitrate melt containing added chloride but no solute salts showed a small cathodic background current, which increased rapidly with applied potentials above -1.1 volts relative to the calomel reference electrode. This rise in current was due to the deposition of the alkali metals from the solvent salt. At -0.1 volt relative to the calomel electrode erratic anodic waves were obtained. Presumably, these resulted from the oxidation of nitrites and lower oxides of nitrogen derived from the thermal de-

composition of the nitrate melt. The cathodic behavior of the ternary salt solvent is shown in Fig. 3.

A search was conducted for ions which would give polarographic waves in the operable range, -0.1 to -1.1 volts. Tests were made on 6 to 12 millimolar solutions of solutes in 30-g. portions of the ternary salt solvent. Chromic chloride hexahydrate, bismuth nitrate pentahydrate, aluminum chloride hexahydrate, zirconyl nitrate dihydrate, titanium potassium fluoride, and gallium trichloride all caused the melt to foam and produced cloudy solutions which yielded erratic current-voltage curves. Thorium nitrate and indium sulfate were sparingly soluble in the melt and yielded no waves. Barium nitrate, praseodymium nitrate, uranyl nitrate hexahydrate, and potassium bromate were all soluble but gave no reduction waves in the operable voltage range. Cupric chloride and thallos nitrate gave clean-cut waves with maxima.

In contrast, cobaltous chloride hexahydrate and potassium chromate gave reduction waves having two and four plateaus, respectively, as shown in Fig. 2. For the cobalt curve the second

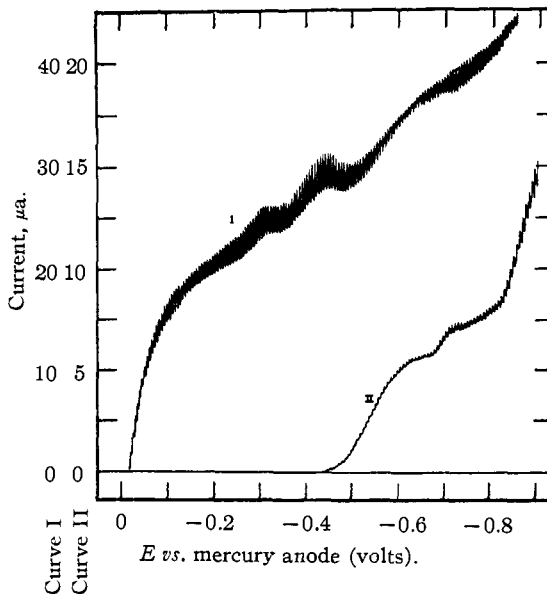


Fig. 2.—Multiple reduction waves in nitrate melt at 153° : I, 7.2 mmole/l. CrO_4^{2-} ; II, 11.8 mmole/l. CoCl_2 .

plateau is 1.3 times as high as the first. The only mechanism consistent with this observation is the oxidation of Co(II) to Co(III) by the nitrate melt with the subsequent reduction of the latter to Co(I) and Co in two stages. According to the Ilkovic equation^{4,5}

$$i_d = 3455nD_s^{1/2}C_s(m/d)^{2/3}t_{max}^{1/6} \quad (2)$$

this interpretation would require a wave height ratio of 1.5, since n would have values of 2 and 3. In Equation (2) i_d is the diffusion current in microamperes, 3455 is a collection of pure num-

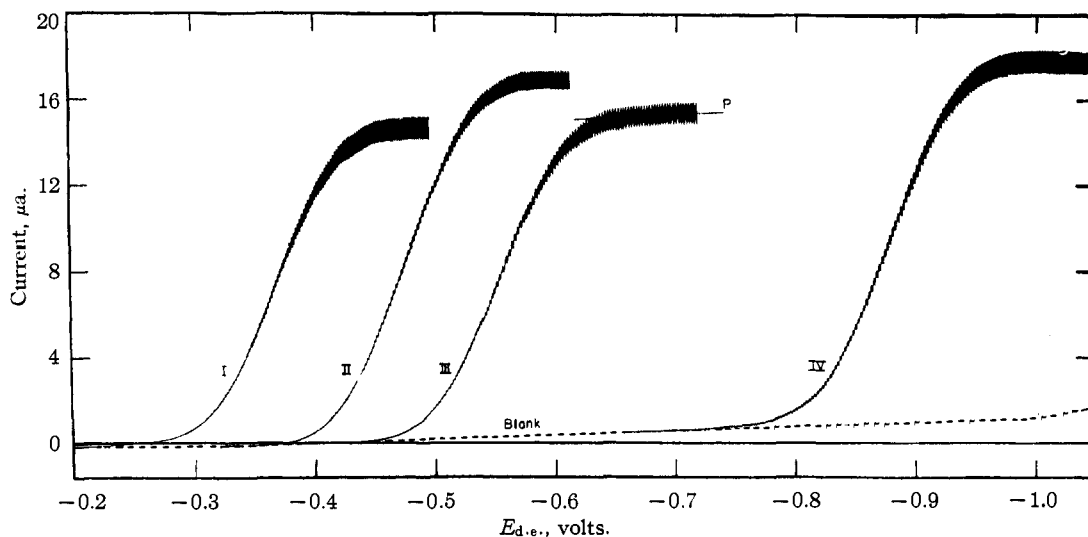


Fig. 3.—Reduction waves in nitrate melt at 160°: I, 8.43 mmole/l. Ni⁺⁺, II, 10.6 mmole/l. Pb⁺⁺; III, 10.6 mmole/l. Cd⁺⁺; IV, 7.71 mmole/l. Zn⁺⁺.

bers and universal constants, n is the number of equivalents involved in the electrode reaction, D_s is the diffusion coefficient of the trace ion in the melt (sq. cm./sec.), C_s is the solute concentration in millimoles per liter, d is the density of the dropping metal, m is the rate of flow of the metal (mg./sec.), and t_{\max} is the average life of the drop in seconds. Hume and Kolthoff⁹ have obtained evidence for the reduction of Co(III) and Co(II) to Co(I) in aqueous cyanide solutions, a finding which lends credence to the postulation of Co(I) in the fused salt. Lingane and Kolthoff¹⁰ found a similar four step reduction of chromate in neutral aqueous solutions with potassium chloride as the supporting electrolyte. They identified the last three waves as the reduction of $\text{CrO}_4^{=}$ to Cr(III), Cr(II), and Cr.

Well defined reproducible waves were found for the reduction of the cations of lead nitrate, nickel nitrate hexahydrate, cadmium nitrate tetrahydrate, zinc nitrate hexahydrate, and manganous chloride tetrahydrate in the ternary salt solution. Since the deposition of manganese occurs at a potential near to that for the alkali metals, quantitative measurements of the diffusion current would have been subject to large errors and were not attempted. Reduction waves for Ni(II), Pb(II), Cd(II), and Zn(II) are shown in Fig. 3, together with the curve for the blank. Diffusion currents were determined from the polarograms by measurement of the height of the straight line, P , through the wave plateau, above the background current at potentials corresponding to the inception of the plateau. Drop times and mercury flow rates were measured at the same potential.

Test of the Ilkovic Equation.—The applicability of the Ilkovic relation, Equation 2, to solutions

(9) D. N. Hume and I. M. Kolthoff, *THIS JOURNAL*, **71**, 867 (1949).

(10) J. J. Lingane and I. M. Kolthoff, *ibid.*, **62**, 852 (1940).

of the ternary salt melt was determined for the reduction of the divalent ions of nickel, lead, cadmium, and zinc at the dropping mercury electrode at 160°. Series of solutions of salts of these metals with concentrations ranging from 1 to 18 millimoles per liter were prepared according to the method described above. The results of experiments performed with cell 1 are shown in Table I.

For a given ion in Table I the ratio $i_d/C_s m^{2/3} t_{\max}^{1/6}$, which is represented by the symbol I, should be constant for a given temperature. This is apparent when the Ilkovic equation is written in the form

$$\frac{i_d}{C_s m^{2/3} t_{\max}^{1/6}} = \frac{3455nD_s^{1/2}}{d^{2/3}} \quad (3)$$

The results indicate that i_d is proportional to $C_s m^{2/3} t_{\max}^{1/6}$, in partial verification of the Ilkovic equation. Since no independent diffusion data exist for ions in the ternary melt it is not possible to evaluate the right-hand side of Equation 3 as a check. However, in view of the success of the Ilkovic equation as applied to other solvents there is little reason to doubt its validity in the present case. With a value of 2 for n and 13.2 g./cc. for the density of mercury at 160° the equation has been used to calculate the diffusion coefficients for the four ions given in Table I.

Attempts to duplicate the results with solutions of the ternary salt prepared at different times led to appreciable variations in the calculated diffusion coefficients for each ion, although internal consistency was obtained in series prepared from the same master salt. It may be that the variations are due to incomplete drying of the salts. Dantuma¹¹ has observed that it is difficult to remove the last traces of water from lithium nitrate at temperatures 100° above its melting

(11) R. J. Dantuma, *Z. anorg. Chem.*, **175**, 1 (1928).

TABLE I

TEST OF THE ILKOVIC EQUATION IN THE TERNARY NITRATE MELT AT 160°

Values in parentheses have been omitted from averages.

Ion	C_s , mmole/l.	m , mg./sec.	t_{max} , sec.	i_d , $\mu A.$	I	$D_s \times 10^6$ cm. ² /sec.
Ni ⁺⁺	1.06	0.868	3.00	1.18	(1.02)	(0.68)
	5.01	.922	3.00	9.18	1.61	1.70
	8.43	.920	2.75	14.7	1.56	1.59
	11.3	.525	3.77	14.8	1.62	1.71
	13.3	.867	2.80	21.4	1.50	1.48
	17.5	.901	2.95	28.8	1.47	1.42
Average					1.55	1.58
Av. dev. %					3.61	6.45
Pb ⁺⁺	1.38	0.650	3.21	1.91	(1.52)	(1.51)
	4.00	.660	3.15	6.20	1.70	1.89
	8.04	.599	2.70	12.3	1.83	2.19
	10.6	.656	3.21	17.2	1.77	2.05
	14.4	.578	3.45	22.6	1.83	2.19
	18.5	.616	2.82	34.5	(2.16)	(3.05)
Average					1.78	2.08
Av. dev. %					2.67	5.05
Cd ⁺⁺	1.17	0.664	3.76	1.72	1.54	1.55
	4.50	.694	2.76	8.92	(2.02)	(2.67)
	7.33	.528	4.63	11.3	1.82	2.16
	10.6	.604	3.68	15.3	1.62	1.72
	13.9	.644	2.54	19.9	1.64	1.76
	17.2	.672	3.60	26.1	1.60	1.68
Average					1.64	1.75
Av. dev. %					4.15	8.22
Zn ⁺⁺	1.17	0.655	3.68	1.60	1.46	1.40
	4.68	0.708	4.10	7.20	1.53	1.53
	7.71	1.53	3.49	16.7	1.32	1.10
	11.2	1.44	3.52	24.7	1.40	1.28
	14.2	1.61	3.31	32.0	1.34	1.18
	18.4	1.62	3.31	44.8	1.45	1.37
Average					1.42	1.31
Av. dev. %					4.46	9.42

point (265°). He suggested that his viscosity measurements of molten lithium nitrate were 18% higher than those of Goodwin and Mailey¹² because the latter investigators did not completely dry their salt. They both agreed upon the viscosities of sodium and potassium nitrates, which are easily dried. In this study the salts were not heated over 220°, to avoid thermal decomposition which gave yellow solutions and erratic current-voltage curves.

Series such as those listed in Table I were partially repeated in three different preparations of the ternary salt, and the over-all average values for the ionic diffusion coefficients are listed in Table II. Tabulated for comparison are diffusion coefficients for the same ions in aqueous solution, calculated from equivalent conductance data with the Nernst relation^{13,14}

$$D_s^0 = RT\lambda^0/zF^2 \quad (4)$$

(12) H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, **26**, 28 (1908).(13) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, page 45.

where D_s^0 is the diffusion coefficient at infinite dilution, R is the gas constant, λ^0 is the limiting equivalent conductance, z is the ionic charge, and F is the faraday. The smaller diffusion coefficients for ions in the melt can be attributed to the higher viscosity of this medium, compared with water. It is interesting to note that the order is the same for the ions in both solvents.

TABLE II

COMPARISON OF IONIC DIFFUSION COEFFICIENTS IN FUSED NITRATE AND WATER SOLUTIONS

Ion	D_s (sq. cm./sec. $\times 10^6$)		
	λ^0 in H ₂ O at 25°	H ₂ O, infinite dilution, 25°	Nitrate melt at 160°C.
Ni ⁺⁺	52	6.9	1.2 \pm 0.2
Pb ⁺⁺	73	9.8	1.8 \pm 0.1
Cd ⁺⁺	54	7.2	1.5 \pm 0.2
Zn ⁺⁺	54	7.2	1.5 \pm 0.2

Diffusion coefficients were calculated from polarograms obtained over the range 160 to 220° for the four ions. The values so obtained were in fair agreement with a temperature dependence of the form

$$D_s = A e^{-E/RT} \quad (5)$$

where A is the usual frequency factor and E is the activation energy for the diffusion process. Activation energies calculated from the data are: Ni(II), 10,000 cal./mole; Pb(II), 13,000 cal./mole; Cd(II), 13,000 cal./mole; and Zn(II), 9,500 cal./mole. These are to be compared with 4,000 to 5,000 cal./mole for most ions in aqueous solution. The greater activation energies in the fused salts can be attributed, in part, to the greater degree of structure which exists in ionic melts over that of aqueous solutions.^{15,16}

Investigation of the Current-Voltage Relation.—Heyrovsky and Ilkovic¹⁷ developed the following equation relating the potential of the dropping electrode, $E_{d.e.}$, and the average current at any point on the current-voltage curve

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF} \ln \left(\frac{i}{i_d - i} \right) \quad (6)$$

where $E_{1/2}$ is the drop potential when $i = i_d/2$ and n is the number of equivalents involved in the electrode reaction. Current-voltage data to verify the above expression were obtained by manually operating the polarograph in a point-by-point manner to avoid errors introduced by the time lag of the recorder when operating continuously on the rising part of the wave. Log $i/(i_d - i)$ is plotted against $E_{d.e.}$ in Fig. 4 for each of the solutions which yielded the polarograms of Fig. 3. Table III presents the current-voltage data for the construction of these plots. From such plots the half-wave potentials can be obtained for values of log $i/(i_d - i)$ equal to zero.

(15) G. W. Stewart, *Trans. Faraday Soc.*, **33**, 238 (1937).(16) E. P. Miller and K. Lark-Horovitz, *Phys. Rev.*, **51**, 61 (1937).(17) J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **7**, 198 (1935).

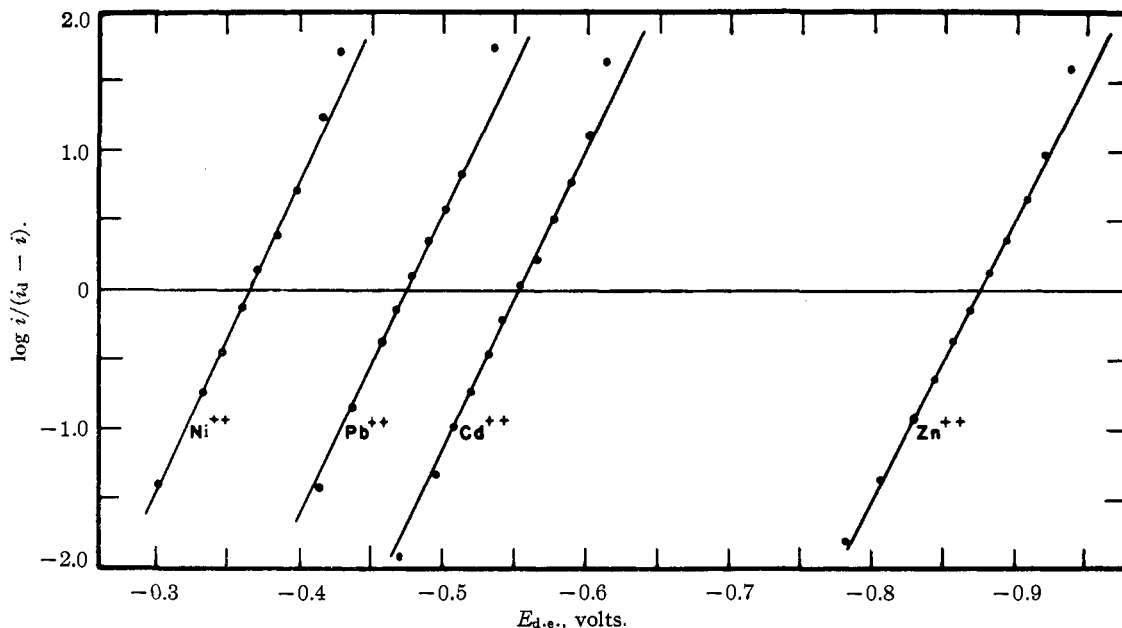


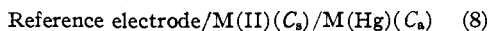
Fig. 4.—Test of current-voltage relation in nitrate melt at 160°.

The half wave potentials so determined for each of the solutions listed in Table I agreed to within a few millivolts for each ion. Reciprocals of the slopes of these and similar curves for Ni(II), Pb(II), and Cd(II) had an average deviation of less than 4% from -0.043 , the theoretical value of the term $-2.303RT/nF$ for 160° and the reduction of divalent ions. The reciprocal slope for the reduction of Zn(II) was -0.050 ± 0.006 . Since the zinc wave lies at the foot of the rising portion of the background current, the currents measured from the polarograms are subject to larger errors and may account for the discrepancy between the experimental and theoretical values for the reciprocal slope.

As a result of developments by Lingane¹⁸ and Stackelberg¹⁹

$$E_{1/2} = E_a^0 - \frac{RT}{nF} \ln \left(\frac{D_s}{D_a} \right)^{1/2} \quad (7)$$

The half wave potentials can thus be related to the diffusion coefficients, D_s , of ions in the melt, and D_a , of metal in the amalgam formed on the drop, and to the standard amalgam potential, E_a^0 , for the cell



C_s is the concentration of reducible ion in the melt and C_a is the amalgam concentration. Standard amalgam potentials were determined in cell 2 of Fig. 1 for amalgams of lead, cadmium, and zinc; nickel is only sparingly soluble in mercury, and was not included. The amalgams were prepared by admixing weighed quantities of the metals and mercury under a stream of hydrogen until solution was complete. They

remained clean as long as oxygen was excluded. Potentials, E_a , of the amalgams in contact with the fused nitrate solutions of the metal ion were measured against the calomel reference electrode. Standard amalgam potentials (referred to the 0.005 mole fraction calomel electrode) at 160° were calculated by means of the Nernst equation

$$E = E_a^0 - \frac{RT}{nF} \ln \frac{\gamma_a C_a}{\gamma_s C_s} \quad (9)$$

The standard state of the amalgam was chosen so that $\alpha/C_a = 1$ when $C_a = 0$. Even the most concentrated amalgam had a solute mole fraction less than 0.002, and the salt solutions were all less than 0.01 molar. The activity coefficients, γ_a and γ_s , were therefore each taken to be unity. Amalgam potentials and calculated values of E_a^0 are listed in Table IV.

Values of $E_{1/2}$, calculated from Equation 7 are compared with the observed values in Table V, and demonstrate the applicability of the Lingane-Stackelberg equation to fused salt polarography. It is of interest to note that nickel has a half wave potential in the fused salt solution that accords more with the electropositive character of nickel than is indicated by its aqueous half wave potential. Kolthoff and Lingane²⁰ attribute the large negative half wave potential to a high activation energy for the deposition of metal from the hexaquo ion. This is consistent with the large value of the slope which they obtained in a plot of $E_{d.e.}$ versus $\log i/(i_d - i)$, and indicates a kind of polarization other than that caused by diffusion. At the higher temperatures which prevail in the fused salt and in the absence of

(18) J. J. Lingane, *THIS JOURNAL*, **61**, 2099 (1939).

(19) M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

(20) I. M. Kolthoff and J. J. Lingane, "Polarography," ref. 14, p. 281.

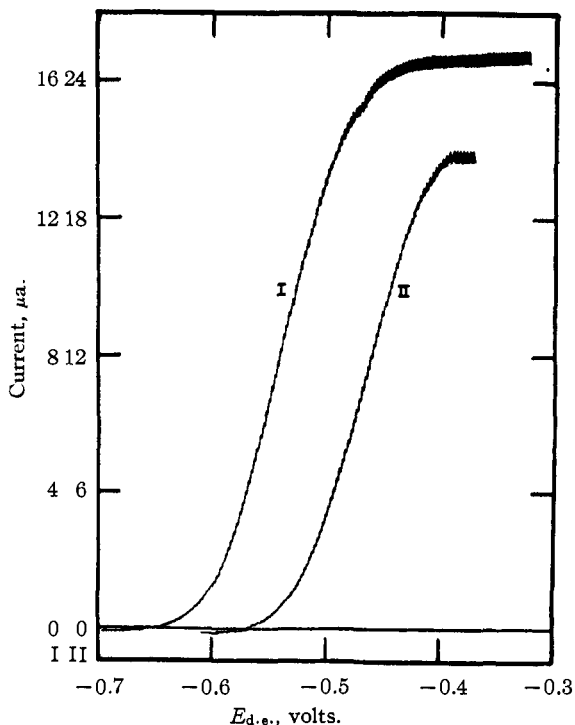


Fig. 5.—Waves for dropping amalgam electrodes in nitrate melt at 160°: I, Cd(Hg), 107 mmole/l.; II, Pb(Hg), 1.61 mmole/l.

from the data of Wogau²² from 99 to 160°. Current-voltage data obtained in the point-wise manner are given in Table VII. Plots of $\log(i_{da} - i)/i$ versus $E_{d.e.}$ are shown in Fig. 6. They are linear and have reciprocal slopes of -0.043 and -0.048 for lead and cadmium, respectively, in fair agreement with the theoretical value of -0.043 . The half wave potentials determined from the dropping amalgam plots

TABLE VII

CURRENT-VOLTAGE RELATION FOR DROPPING AMALGAM ELECTRODES IN NITRATE MELT AT 160°

Lead amalgam $C_a = 1.61$ mmole/l.			Cadmium amalgam $C_a = 1.07$ mmole/l.		
$E_{d.e.}$ volts	i μA	$\log \frac{i_{da} - i}{i}$	$E_{d.e.}$ volts	i μA	$\log \frac{i_{da} - i}{i}$
-0.542	-0.30	1.81	-0.619	-0.30	1.72
- .514	- 1.65	1.04	- .589	- 1.20	1.09
- .488	- 4.96	0.47	- .564	- 3.90	0.50
- .468	- 9.16	0.06	- .541	- 7.71	0.04
- .446	-15.0	-0.51	- .518	-11.8	-0.44
...	-19.7 ^a	...	- .492	-14.5	-0.96
- .468 ^b	- .464	-15.6	-1.49
.043 ^c	-16.1 ^a	...
			- .538 ^b
		
			.048 ^c

^a Limiting diffusion current, i_{da} . ^b Half-wave potential, $E_{1/2}$. ^c Negative reciprocal of slope of $\log(i_{da} - i)$ vs. $E_{d.e.}$

(22) M. v. Wogau, *Ann. Physik*, **23**, 345 (1907).

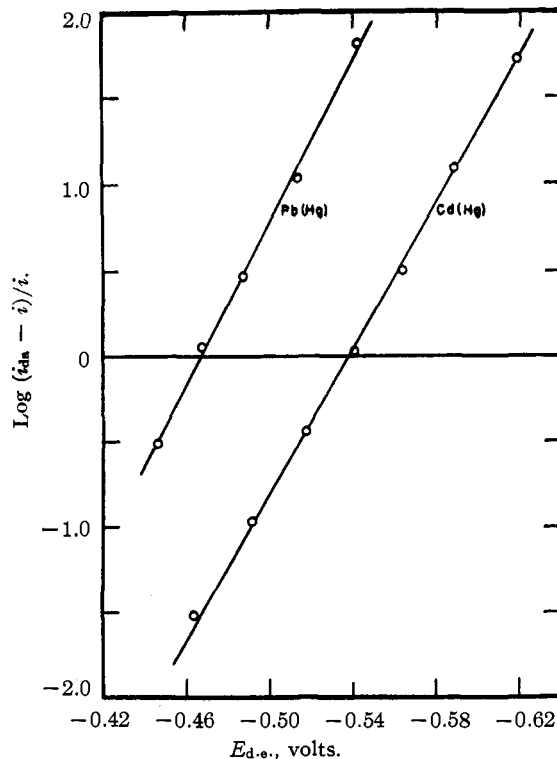


Fig. 6.—Current-voltage relation for dropping amalgam electrodes.

are -0.468 and -0.538 volt for lead and cadmium. These values may be compared with -0.473 and -0.549 volt, obtained from the reduction waves of lead and cadmium ions, respectively. The half wave potentials for the oxidation and reduction waves should be the same, as given by Equation 7.

Dropping Lead, Bismuth and Silver Electrodes.—As noted earlier, one of the objectives of the study was to apply dropping metal electrodes to liquid systems at high temperatures for the purpose of obtaining ionic diffusion coefficients, electrode potentials and, perhaps, analytical data. Lead and bismuth dropping electrodes in a lithium chloride-potassium chloride eutectic at 450 to 500° became inoperable after a few moments because of stoppage of the Pyrex capillaries. The capillaries were of the type used for the dropping amalgam study (Fig. 1).

A dropping silver electrode in a quartz capillary gave a linear current-voltage relationship when used in molten sodium chloride at 1000°. A range of anodic to cathodic potentials was applied to the dropping electrode relative to a pool of silver which functioned as the unpolarized electrode. The sodium chloride assumed a reddish-brown color, and an aqueous solution of the cooled melt had a higher pH than sodium chloride which had not been electrolyzed. Lorenz and Winzer²³

(23) R. Lorenz and R. Winzer, *Z. anorg. allgem. Chem.*, **183**, 121 (1929).

found that the solubility of metallic sodium in molten sodium chloride is 15 to 20% at 850° and increases with increasing temperature; moreover, the color of the solutions was reddish-brown. No silver chloride was found when the polarographic melt was dissolved in water, so that reduction of the alkali metal chloride was not caused by silver metal. It appears that sodium chloride was electrolyzed even at very low applied potentials to yield metallic sodium. No gas evolution was observed at the anode. The electrolysis current was large, making polarography for trace constituents in such a solution impossible.

A dropping silver electrode in a borax melt gave a much lower background current, but little could be obtained from the erratic polarograms because of the rapid attack on the quartz capillary by the melt.

Acknowledgments.—The authors wish to acknowledge the helpful advice of Drs. O. J. Kleppa, T. Rosenqvist and W. M. Saltman, and Mr. R. E. Fryxell of this laboratory.

Summary

1. Typical polarographic waves have been obtained for the reduction of a number of cations

at the dropping mercury electrode in a melt of lithium, sodium, and potassium nitrates.

2. The Ilkovic equation has been found to apply for the reduction of the divalent ions of nickel, lead, cadmium, and zinc in the ternary nitrate melt at 160°.

3. The theory of the current-voltage relation has been experimentally confirmed in the nitrate melt for the cations mentioned above. Half wave potentials calculated from experimentally determined amalgam potentials for lead, cadmium, and zinc were in good agreement with the observed values.

4. Dropping lead and cadmium amalgam electrodes in the nitrate melt yielded anodic waves whose half wave potentials agreed with those for the reduction waves of the corresponding ions. Diffusion coefficients for lead and cadmium in mercury at 160° were calculated from the Ilkovic equation by the use of the anodic diffusion currents obtained with dropping amalgam electrodes.

5. Attempts to operate dropping electrodes of pure lead and bismuth in a molten lithium chloride-potassium chloride melt were unsuccessful. Dropping molten silver electrodes gave no useful polarograms in sodium chloride or borax at 1000°.

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The Direct Determination of the Critical Temperature and Critical Pressure of Normal Hydrogen¹

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Introduction

The earliest determinations of the critical pressure and critical temperature of hydrogen were made by Olszewski^{2,3} who first reported the critical pressure as 20 atmospheres and the critical temperature as -234.5°, but later gave them as 13.4 to 15.0 atmospheres and as -240.8°, respectively. Dewar^{4,5,6} obtained values ranging from 15.0 to 19.4 atmospheres and from -221 to -243°. Bulle⁷ obtained values of 11.0 atmospheres and -241.15°, respectively. Although he used a direct method, his data suffered from the presence of rather severe temperature gradients in his apparatus.

The values generally accepted today are those determined, indirectly, at Leiden⁸ from extrapolation of *PV* isotherms in the neighborhood of the

critical point, in conjunction with the vapor pressure curve. Their values of the critical pressure and temperature are 12.80 atmospheres and -239.92°,⁹ respectively. A complete summary of the investigations on critical phenomena for hydrogen has been given by Pickering.¹⁰

We have designed and constructed an apparatus for accurate direct measurements of critical temperature and pressure. This work has seemed worthwhile because of the need for accurate values of the critical constants in correlating reduced equations of state for pure gases and gaseous mixtures¹¹ with such molecular properties as intermolecular potentials and collision diameters. Additional interest in critical phenomena has been aroused by theories of condensation in the critical region recently advanced by Mayer¹² and by Rice.¹³ Our first data, with the new apparatus, has been taken on hydrogen.

(1) This work was supported in part by the Air Materiel Command under Contract with The Ohio State University.

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