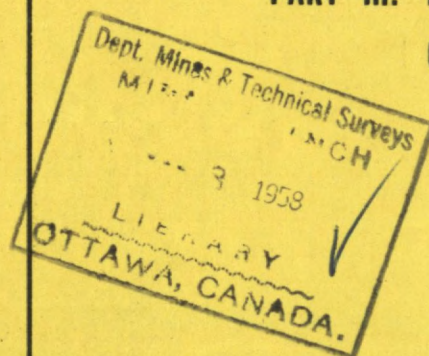CANADA

VOLTAIC CELLS IN FUSED SALTS

PART III. THE SYSTEM SILVER-SILVER CHLORIDE, CADMIUM-CADMIUM CHLORIDE

by

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PART III. THE SYSTEM SILVER – SILVER CHLORIDE, CADMIUM – CADMIUM CHLORIDE[1]

S. N. FLENGAS[2] AND T. R. INGRAHAM

ABSTRACT

Using a silver – silver chloride reference electrode, the standard electrode potential has been established for the equilibrium Cd|Cd++ in melts containing equimolar quantities of KCl and NaCl. The experimentally obtained standard potential was greater than that calculated from theoretical thermodynamic data. This difference was attributed to the formation of a cadmium complex in the melt. A dissociation constant for the complex was calculated.

The effect of temperature on the electromotive force of the silver–cadmium voltaic cell was also measured, and the heat of the cell reaction was calculated from the data. To extend the temperature range of the cadmium data, a cadmium–lead alloy was used in the higher temperature experiments. To correlate these data with those for the pure cadmium system, the activity coefficients of cadmium in the alloy were determined electrometrically using the silver – silver chloride electrode as a reference. It was found that the activity coefficients were in agreement with previously published data obtained at lower temperatures using a pure cadmium reference electrode. The activity coefficients were virtually independent of temperature but showed large positive deviations from unity when the mole fraction of cadmium was decreased below about 0.8.

INTRODUCTION

Parts I and II of this series (1, 2) described the development and use of a reversible silver – silver chloride reference electrode for determining the electromotive forces of voltaic cells in chloride melts at high temperatures.

In this paper, experiments will be described in which the silver – silver chloride reference electrode was used to study the cadmium – cadmium chloride equilibria. An equimolar mixture of molten potassium and sodium chlorides was used as the common solvent.

These results are an additional contribution to the current program of establishing electromotive series for metals in molten salts at different temperatures.

EXPERIMENTAL

The technique used to study the Cd–Ag system was essentially the same as that previously described (1). During the preliminary experimental work it became apparent that because of the relatively high vapor pressure of molten cadmium and the inflammability of cadmium vapor in air, a closed cell operating with an inert atmosphere would be required. The complete cell design is shown in Fig. 1. The cell was constructed from silica tubing of 2 in. diameter and consisted of two sections connected by a ground silica joint. The upper section of the cell was closed with a cork stopper, into which were fitted the silver – silver chloride reference electrode, the thermocouple well, the feeding pipe with stirrer, and the gas inlet tube. The cork stopper was covered externally with Pyseal cement and then water-cooled to prevent the melting of the cement from the heat of the furnace. The inner surface of the cork stopper was covered with a close-fitting layer of asbestos. The lower section of the cell was used as a container for the molten metal indicator electrode and the molten salts. Electrical contact with the indicator electrode was made by means of a tungsten wire sealed into silica tubing and dipped into the metal pool.

Argon outlet

Feeding tube
with stirrer

Argon inlet

Platinum wire reference
Electrode connection

Tungsten wire
indicator electrode
connection

Thermocouple well

Water outlet

Pyseal cement cover
Cork
Asbestos layer
Water inlet

Water jacketed
cooling system

Furnace level

24"

Ag/AgCl Reference
Electrode

Cd Cl₂ in ½ mole
K Cl-NaCl melt
solvent

Asbestos fibre sealed
into silica
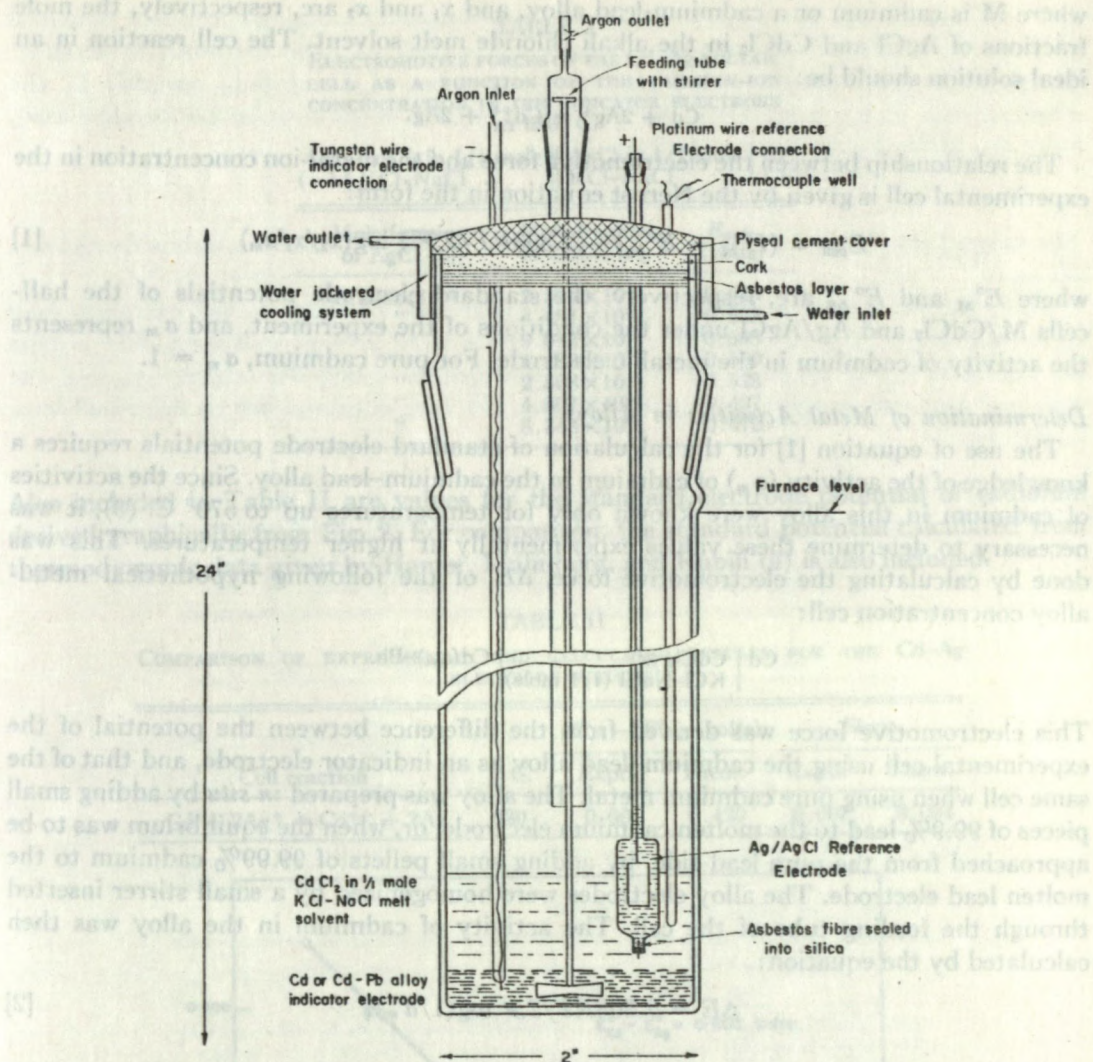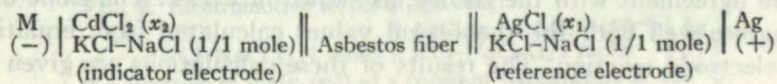
Cd or Cd-Pb alloy
indicator electrode

2"

FIG. 1. All silica cell.

For potential measurements at temperatures below the boiling point of cadmium (767° C.), the indicator electrode was either pure molten cadmium metal or cadmium–lead alloy. At temperatures above 767° C., a high boiling point cadmium–lead alloy was used to determine the electromotive forces over a range of temperature in excess of 100 Centigrade degrees and thus clearly establish the linearity of the data.

To protect the contents of the cell from the atmosphere, purified argon was introduced continuously into the cell and released through a small Bunsen valve. The slight positive pressure of argon in the cell protected the contents completely over the full course of runs lasting up to 2 days.

The voltaic cell used during the experiments may be represented as follows:

M | CdCl₂ (x₂) ‖ Asbestos fiber ‖ AgCl (x₁) | Ag
(−) | KCl–NaCl (1/1 mole) ‖ ‖ KCl–NaCl (1/1 mole) | (+)
(indicator electrode) (reference electrode)

where M is cadmium or a cadmium-lead alloy, and x_1 and x_2 are, respectively, the mole fractions of AgCl and $CdCl_2$ in the alkali chloride melt solvent. The cell reaction in an ideal solution should be:

$$Cd + 2Ag^+ = Cd^{++} + 2Ag.$$
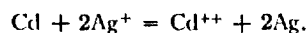
The relationship between the electromotive force and the metal-ion concentration in the experimental cell is given by the Nernst equation in the form:

$$E_{cell} = (E°_M - E°_{Ag}) - (2.303RT/2\mathscr{F}) \log(x_2/x_1^2 a_m) \qquad [1]$$

where $E°_M$ and $E°_{Ag}$ are, respectively, the standard electrode potentials of the half-cells $M/CdCl_2$ and Ag/AgCl under the conditions of the experiment, and a_m represents the activity of cadmium in the metallic electrode. For pure cadmium, $a_m = 1$.

Determination of Metal Activities in Alloys

The use of equation [1] for the calculation of standard electrode potentials requires a knowledge of the activity (a_m) of cadmium in the cadmium-lead alloy. Since the activities of cadmium in this alloy were known only for temperatures up to 570° C. (3), it was necessary to determine these values experimentally at higher temperatures. This was done by calculating the electromotive force, ΔE, of the following hypothetical metal-alloy concentration cell:

$$Cd \ \left| \begin{matrix} CdCl_2 \ (x) \\ KCl-NaCl \ (1/1 \ mole) \end{matrix} \right| \ Cd(a_m)-Pb.$$
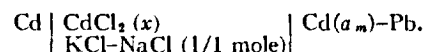
This electromotive force was derived from the difference between the potential of the experimental cell using the cadmium-lead alloy as an indicator electrode, and that of the same cell when using pure cadmium metal. The alloy was prepared *in situ* by adding small pieces of 99.9% lead to the molten cadmium electrode, or, when the equilibrium was to be approached from the pure lead side, by adding small pellets of 99.99% cadmium to the molten lead electrode. The alloy electrodes were homogenized by a small stirrer inserted through the feeding tube of the cell. The activity of cadmium in the alloy was then calculated by the equation:

$$\Delta E = 2.303RT/2\mathscr{F} \log(1/a_m). \qquad [2]$$

RESULTS AND DISCUSSION

The electromotive force of the cadmium cell was measured first as a function of the metal-ion concentration and then as a function of temperature. The results of the experiments in which the concentration of the metal ion was varied at constant temperature are shown in Table I.

From equation [1] it follows that the relationship between E_{cell} and $\log(x_2/x_1^2)$ should be linear; and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{cell} = E°_M - E°_{Ag}.$$

When the electromotive forces of the cells were plotted against $\log(x_2/x_1^2)$, as calculated from the experimental data given in Table I, the results were well represented by a straight line in agreement with the theory, as shown in Fig. 2. The slope of the experimental line agrees well with the theoretical values calculated from equation [1] for a two-electron electrode reaction. The results of these calculations are given in Table II.

TABLE I

ELECTROMOTIVE FORCES OF THE Cd–Ag VOLTAIC
CELL AS A FUNCTION OF THE CADMIUM-ION
CONCENTRATION IN THE INDICATOR ELECTRODE
AT 680° C.

Cd | CdCl$_2$ in 1/1 mole	AgCl in 1/1 mole | Ag	
(−) | KCl–NaCl	KCl–NaCl | (+)	

Mole fraction of AgCl (x_1)	Mole fraction of CdCl$_2$ (x_2)	E_{cell} (volts)
6.235×10^{-2}	2.309×10^{-3}	0.625
''	4.481×10^{-3}	0.598
''	9.047×10^{-3}	0.568
''	1.488×10^{-2}	0.550
''	2.568×10^{-2}	0.528
''	4.807×10^{-2}	0.497
''	8.348×10^{-2}	0.472

Also included in Table II are values for the standard electrode potential of cadmium derived graphically from Fig. 2. For comparison, the standard potential calculated from thermodynamic data given by Hamer, Malmberg, and Rubin (4) is also included.

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS FOR THE Cd–Ag
ELECTRODE SYSTEMS

Cell reaction	$t°$ C.	$E°_M − E°_{Ag}$ (volts)		Slope	
		Exptl.	Theor.	Exptl.	Theor.
Cd + 2Ag$^+$ = Cd^{++} + 2Ag	680	0.604	0.420	0.097	0.094

FIG. 2. Electromotive forces of the cells:

Cd \| CdCl$_2$ \| AgCl (x_1 = 6.235×10^{-2}) \| Ag
(−) \| KCl–NaCl (1/1 mole) \| KCl–NaCl (1/1 mole)   \| (+)

as a function of $\log(x_2/x_1^2)$ at a constant temperature of 680° C.
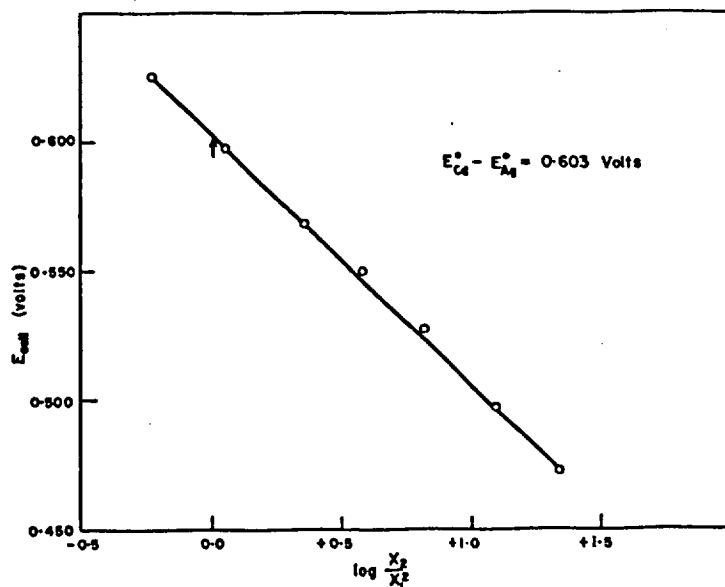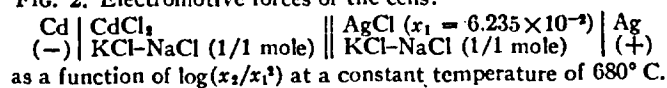
It is of theoretical interest to compare the experimentally obtained standard potential of the voltaic cell with the theoretical value calculated from the thermodynamic data. If the difference is entirely attributed to the presence of a cadmium complex in the alkali chloride melt solvent, the dissociation constant, K_d, of the complex can be calculated, using the method previously described (1):

$$K_d \text{ (Cd complex)} = 1.17 \times 10^{-2}.$$

The magnitude of this value indicates the presence of a fairly stable cadmium complex in the melt.

The effects of temperature change on the electromotive forces of the cadmium–lead alloy – silver and the cadmium–silver voltaic cells were investigated next. The results are shown in Table III and Fig. 3. (The procedure by which the activity a_m and the standard electrode potentials included in Table III were obtained will be described later in the text.)

TABLE III

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELLS

(a)   Cd | CdCl$_2$ ($x_2 = 3.875 \times 10^{-2}$) || AgCl ($x_1 = 6.103 \times 10^{-2}$) | Ag
       (−) | KCl–NaCl (1/1 mole) || KCl–NaCl (1/1 mole) | (+)

T (° K.)	E_{cell} (volts)
933	0.5255
955	0.5132
980	0.5015
1000	0.4921
1025	0.4784

(b)   Cd(a_m)–Pb | CdCl$_2$ ($x_2 = 3.785 \times 10^{-2}$) || AgCl ($x_1 = 6.103 \times 10^{-2}$) | Ag
       (−) | KCl–NaCl (1/1 mole) || KCl–NaCl (1/1 mole) | (+)

where $x_m = 0.4754$ and $a_m = 0.7654$

T (° K.)	On heating E_{cell} (volts)	$E°_{Cd} - E°_{Ag}$ (volts)	T (° K.)	On cooling E_{cell} (volts)	$E°_{Cd} - E°_{Ag}$ (volts)
982	0.493	0.568	1025	0.456	0.537
984	0.479	0.557	1011	0.463	0.544
991	0.474	0.553	997	0.472	0.552
1012	0.466	0.546	985	0.476	0.555
1033	0.454	0.536	973	0.482	0.560
1065	0.438	0.523	957	0.490	0.565
1084	0.432	0.518	947	0.494	0.569
			937	0.498	0.572
			935	0.502	0.576

It is of interest to note, in Fig. 3, that the two straight lines which express the relationship between the electromotive force of the foregoing cells and temperature are essentially parallel. This shows that the activity of cadmium in a cadmium–lead alloy is almost independent of temperature. The results of experiments to determine the activities a_m of cadmium in a cadmium–lead alloy at one temperature (680° C.) are shown in Table IV. The activity coefficients were calculated using the well-known equation:
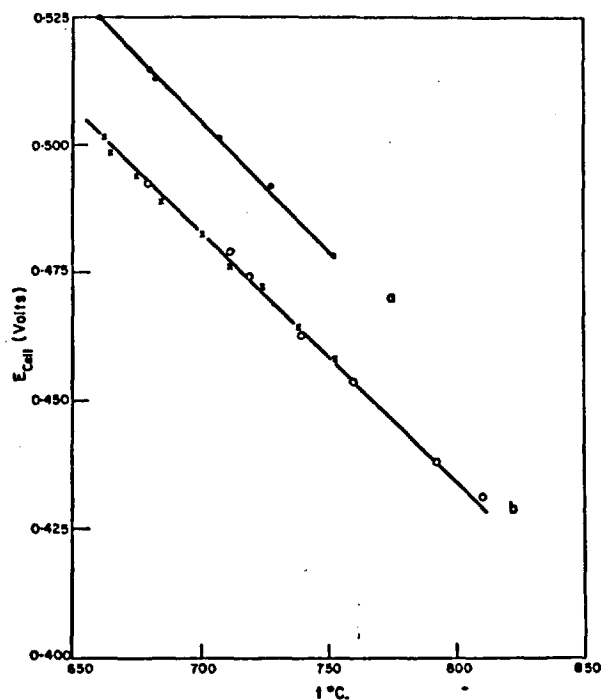
$$a_m = x_m \gamma_m \qquad\qquad [3]$$
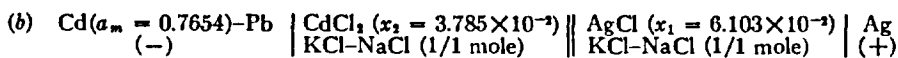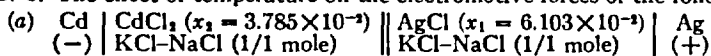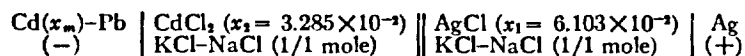
FIG. 3. The effect of temperature on the electromotive forces of the following cells:

(a) Cd | CdCl$_2$ (x_2 = 3.785$\times$10^{-2}) || AgCl (x_1 = 6.103$\times$10^{-2}) | Ag
     (−) | KCl–NaCl (1/1 mole) || KCl–NaCl (1/1 mole) | (+)

(b) Cd(a_m = 0.7654)–Pb | CdCl$_2$ (x_2 = 3.785$\times$10^{-2}) || AgCl (x_1 = 6.103$\times$10^{-2}) | Ag
              (−) | KCl–NaCl (1/1 mole) || KCl–NaCl (1/1 mole) | (+)

O with increasing temperature, $\times$ with decreasing temperature.

TABLE IV

MEASUREMENTS OF THE ACTIVITY OF CADMIUM METAL IN THE
CADMIUM–LEAD ALLOY AT 680° C.

Cd(x_m)–Pb | CdCl$_2$ (x_2 = 3.285$\times$10^{-2}) || AgCl (x_1 = 6.103$\times$10^{-2}) | Ag
     (−) | KCl–NaCl (1/1 mole) || KCl–NaCl (1/1 mole) | (+)

Mole fraction of cadmium (x_m)	E_{cell} (volts)	ΔE (volts)	Activity (a_m) of cadmium metal in the alloy	Activity coefficient (γ_m)
1.000	0.4985	−0.0000	1.0000	1.000
0.9495	0.4956	−0.0029	0.9315	0.981
0.8602	0.4920	−0.0065	0.8535	0.992
0.7873	0.4900	−0.0085	0.8128	1.032
0.6883	0.4916	−0.0069	0.8453	1.228
0.5664	0.4910	−0.0075	0.8537	1.507
0.4718	0.4878	−0.0107	0.7709	1.634
0.4712	0.4870	−0.0115	0.7551	1.602
0.3426	0.4768	−0.0217	0.5889	1.719
0.2331	0.4665	−0.0320	0.4585	1.967
0.1434	0.4524	−0.0461	0.3251	2.266
0.0801	0.4353	−0.0632	0.2143	2.675

where x_m is the mole fraction of cadmium in the alloy and γ_m is the activity coefficient.

In Table IV it can be seen that at high cadmium concentrations the cadmium–lead

alloy behaves essentially ideally. Below a mole fraction of about 0.8, deviations from ideality increase and activity coefficients greater than unity are obtained.

The variation of the activity with the mole fraction of cadmium in the cadmium-lead alloy is shown in Fig. 4.
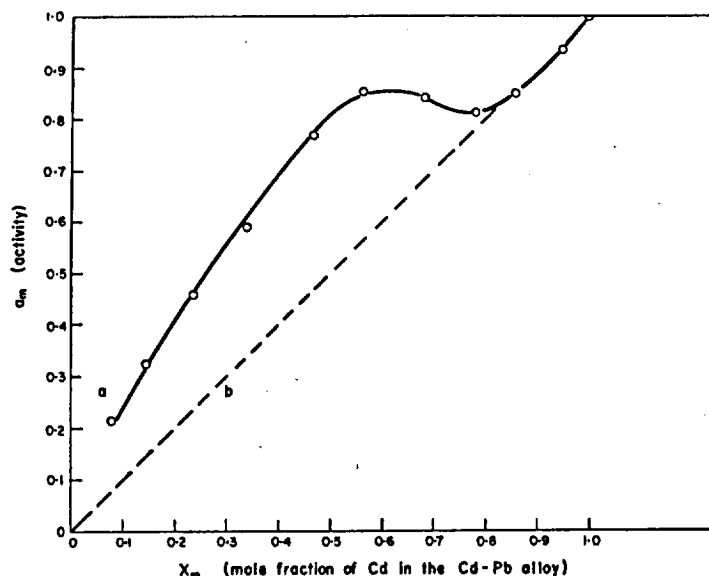

FIG. 4. The variation of the activity of cadmium in the Cd–Pb alloy, with the mole fraction of cadmium at 680° C. (a) Experimental data; (b) theoretical line for an ideal alloy.

· The activity coefficient values obtained in the present investigation for a temperature of 680° C. are in good agreement with values given in the literature for lower temperatures. This is shown in Table V, where activity coefficients calculated from the data given by Taylor (3) are tabulated together with values obtained in the present investigation.

TABLE V

ACTIVITY COEFFICIENTS OF CADMIUM METAL IN CADMIUM–LEAD ALLOY AT VARIOUS TEMPERATURES AND CONCENTRATIONS

Mole fraction of cadmium in the alloy	Activity coefficient (γ_m)				
	432° C.	480° C.	544° C.	572° C.	680° C.*
0.2	2.50	2.35	2.15	2.10	2.50
0.4	1.75	1.68	1.58	1.57	1.65
0.6	1.48	1.48	1.44	1.44	1.50

*Values obtained in the present investigation.

It will be observed that temperature change has a very small effect on the values of the activity coefficients. This is in agreement with the previous observations on temperature effects in Fig. 3. The two lines are essentially parallel and the difference between the, values of the respective electromotive forces corresponds to a $(2.303RT/2\mathscr{F})\log a_m$ term, where a_m is the activity of the cadmium in the alloy at the lower temperature of 680° C.

Having established the activities of cadmium in a cadmium–lead alloy, it was possible to use equation [1] to calculate the standard electrode potential of cadmium ($E°_{Cd} - E°_{Ag}$) at different temperatures from the data in columns 1 and 2 of Table III(b). From these standard potentials, using the well-known equations

$$\Delta F° = -nE°\mathscr{F}, \tag{4}$$

$$\Delta F° = -2.303RT \log K,$$

the equilibrium constant for the cell reaction given in Table II was calculated for various temperatures. The results of these calculations are shown in Fig. 5, where log K was plotted against the reciprocal of the absolute temperature. The curve is linear over the
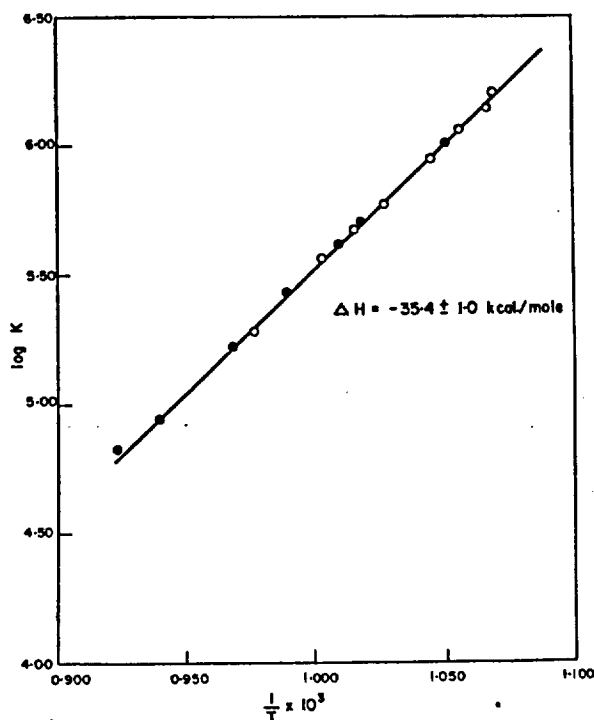

FIG. 5. The variation of log K with the reciprocal of temperature for the system:
Cd($a_m = 0.7654$)–Pb | CdCl$_2$ ($x_2 = 3.785 \times 10^{-2}$) ‖ AgCl ($x_1 = 6.103 \times 10^{-2}$) | Ag
(−) | KCl–NaCl (1/1 mole)   ‖ KCl–NaCl (1/1 mole) | (+)
O with increasing temperature, ● with decreasing temperature.

temperature range investigated, and the best straight line through the experimental points was calculated by applying the least squares method. The heat of reaction (ΔH_r), which is the difference between the heats of formation of the respective chlorides in the melt solvent, i.e.

$$\Delta H_r = \Delta H_{f(CdCl_2 \text{ in } KCl-NaCl)} - \Delta H_{f(AgCl \text{ in } KCl-NaCl)}, \tag{5}$$

can be calculated from the slope of the straight line in Fig. 5, in accordance with the van't Hoff equation,

$$d \ln K/dT = \Delta H_r/RT^2. \qquad [6]$$

The result·thus obtained is:

$$\Delta H_r = -35.4 \pm 1.0 \text{ kcal.}$$

It will be noted that this value includes any effect due to the presence of the solvent.

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