VOLTAIC CELLS IN FUSED SALTS

PART I. THE SILVER-SILVER CHLORIDE, COBALT-COBALTOUS CHLORIDE SYSTEM

CANADA

by

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MINERAL DRESSING AND PROCESS METALLURGY DIVISION

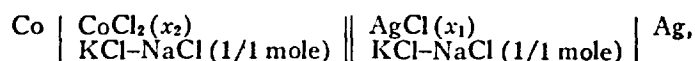PRICE 25 CENTS

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PART I. THE SILVER – SILVER CHLORIDE, COBALT – COBALTOUS CHLORIDE SYSTEM[1]

S. N. FLENGAS[2] AND T. R. INGRAHAM[3]

ABSTRACT

A reversible silver – silver chloride reference electrode for use in melts at high temperatures has been developed. It was found that the solution of silver chloride in an equimolar mixture of KCl–NaCl melt is ideal for the range of concentrations studied, i.e. 1.0×10^{-3} to 6.0×10^{-2} mole fraction of AgCl.

The electromotive force of the voltaic cell

$$\text{Co} \left| \begin{array}{c} \text{CoCl}_2(x_2) \\ \text{KCl–NaCl (1/1 mole)} \end{array} \right\| \begin{array}{c} \text{AgCl}(x_1) \\ \text{KCl–NaCl (1/1 mole)} \end{array} \right| \text{Ag,}$$

in which the half-cell to the right contains the above-mentioned reference electrode, was measured as a function of CoCl_2 concentration. The applicability of the Nernst equation to this system was established. Deviation from ideality was observed in the case of the solution of CoCl_2 in the melt solvent, and this was attributed to the formation of a complex. The dissociation constant of this complex was calculated as 4.50×10^{-3} at 710° C.

The effect of temperature on the electromotive force of this cell was also measured, and the heat of the cell reaction in the presence of solvent ($\text{Co} + 2\text{AgCl} \rightarrow \text{CoCl}_2 + 2\text{Ag}$) was calculated from the data as 22.8 ± 1.3 kcal.

The thermodynamic significance of the standard electrode potential of the Co–Ag voltaic cell, derived experimentally as 0.324 volt, is discussed briefly.

INTRODUCTION

The electrochemistry of ionic discharge at electrodes in aqueous solutions has been well worked out over a period of years, and extensive tabulations of experimental electrode potentials based on the hydrogen scale are available.

On the other hand, recent metallurgical studies on electrowinning in molten salts have emphasized the almost complete lack of experimental data on the reversible discharge potentials of ions in media such as molten alkali and alkali earth chlorides, and their mixtures, particularly at high temperature.

Almost all the available data in this field, including the pioneer work of Lorenz (9), consist of values for the decomposition potentials of electrolytic cells containing molten salt electrolytes, and electromotive forces of concentration cells with (1, 5) and without (10, 11, 12, 13, 16) transference.

The few attempts which have been made to measure the electrode potential of metals in solutions of their ions in molten salts have been restricted to rather low temperature melts, and were only partly successful owing to the difficulty of constructing a reversible reference electrode which would be both simple to handle and stable.

This paper is the first in a series which will describe experiments done at the Mines Branch to establish an electrochemical series in melts under equilibrium conditions, and to calculate the related thermodynamic data from electromotive force measurements on voltaic cells. As an initial step, a reversible electrode for high temperatures has been developed and used to determine the potentials of a cobalt – cobaltous chloride half-cell under varying conditions of concentrations and temperature.

In subsequent publications in this series, similar data will be reported for other metals.

A. THE DEVELOPMENT OF A HIGH TEMPERATURE Ag–AgCl REFERENCE ELECTRODE

Several types of reference electrodes for use in fused systems have been introduced recently (2, 3, 4, 14, 15). Senderoff and Brenner (14) have described an Ag–AgCl reference electrode constructed in pyrex glass, in which free diffusion and mixing of the solutions were hindered by means of a coarse asbestos plug. This cell, however, was not completely free from the effects of diffusion and it introduced into the measurements an unknown boundary potential. Delimarski *et al.* (3, 4) used half-cells of the type

$$\text{Na} \left| \begin{array}{c} \text{amalgamated with Hg} \\ \text{or other metals} \end{array} \right\| \text{Na–glass diaphragm} \left\| \text{Na melt} \right.$$
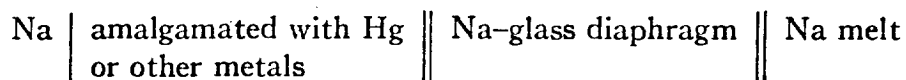
and measured the electrode potentials of several metals.

A modification of this electrode is that introduced recently by Bockris *et al.* (2), in which the sodium amalgam was replaced by an Ag–AgCl (KCl, LiCl) electrode. Unfortunately, by the nature of its construction, the use of this type of reference electrode is confined to low temperatures. Furthermore, electrodes of this type are not amenable to an exact thermodynamic treatment and, hence, cannot be used in establishing the equilibria in chemical reactions taking place in an electrolytic cell, except in the case of concentration cells.

Experimental

In the present investigation, as the result of studying a number of different cell designs, the following type of reference electrode was adopted:

$$\text{Ag} \left| \begin{array}{c} \text{AgCl } (x) \\ \text{KCl–NaCl (1/1 mole)} \end{array} \right\| \text{Asbestos fiber}$$
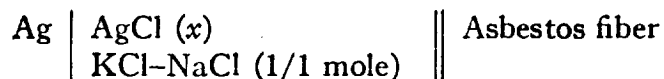
The half-cell was constructed from silica tubing and is essentially a modification of a low temperature reference electrode developed by Flengas and Rideal (5) for measuring the electromotive forces of concentration cells in fused alkali nitrate melts. The design of the half-cell is shown in Fig. 1 *a*. Very pure silver foil (99.999%) was spot-welded to a platinum wire for the electrical contact and, before use, it was cleaned with acetone and inserted in the molten solution of AgCl in 1/1 mole KCl–NaCl in the half-cell. To prepare this solution, Analar grade salts KCl and NaCl were used. AgCl was prepared from the corresponding nitrate salt. The mole fraction (x) of AgCl in the reference half-cell, unless otherwise stated, was 6.103×10^{-2} (which corresponds to about 1 mole of AgCl per 1000 g. of KCl–NaCl mixture).
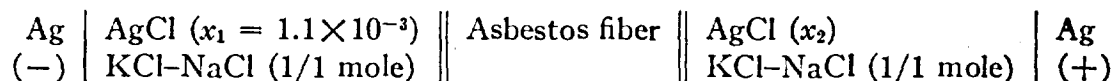
The metallic silver electrode, apart from being completely immersed in the melt, did not require any special protection from air, since it is known that Ag_2O decomposes at 300° C. and, therefore, this metal at high temperature always presents a clean surface (8).

Electrical contact between the solutions in the standard cell and the indicator electrode was made through an asbestos fiber sealed into the end of the side-arm tube of the reference. To obtain a good seal between the asbestos and silica, the silica tubing was first drawn down to about 3 mm. I.D. and then the asbestos fiber, taken from an asbestos rope, was inserted and heated until all organic matter contained in it had been burned. The narrow part of the tube was then heated in a hydrogen flame, care being taken to avoid fusion of the asbestos with the silica. This was feasible only when the asbestos fiber was hanging in the center of the tubing and was not in contact with the walls.

Finally, when the silica was uniformly pliable, the flame was withdrawn and the sides of the tube were pressed into contact with the asbestos fiber, using platinum-foil-covered pliers.

It was found that a half-cell reference having about 1.5 cm. of asbestos sealed into the end of the silica side-arm could be used for several weeks with the potential remaining constant within 1 mv. A 10,000 ohm resistor was connected in series with the electrode to ensure that during operation only very small currents could be drawn through the cell, thus preventing changes in concentration.

The applicability of the Nernst equation to the Ag–AgCl(x) system, and the reversibility of the system, were first investigated by measuring the electromotive forces of the following concentration cells:

$$\text{Ag} \left| \begin{array}{c} \text{AgCl } (x_1 = 1.1 \times 10^{-3}) \\ \text{KCl–NaCl (1/1 mole)} \end{array} \right\| \text{Asbestos fiber} \left\| \begin{array}{c} \text{AgCl } (x_2) \\ \text{KCl–NaCl (1/1 mole)} \end{array} \right| \text{Ag}$$
$$(-) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (+)$$

As written above, the half-cell to the left was the reference electrode as described previously, and the half-cell to the right contained the indicator electrode, which in this case was a long silver wire spot-welded to a platinum wire lead. The container for the solution of the indicator electrode consisted of a 250 ml. silica beaker placed in a tubular electric furnace. The entire apparatus is shown in Fig. 1. During a run, oxygen-free
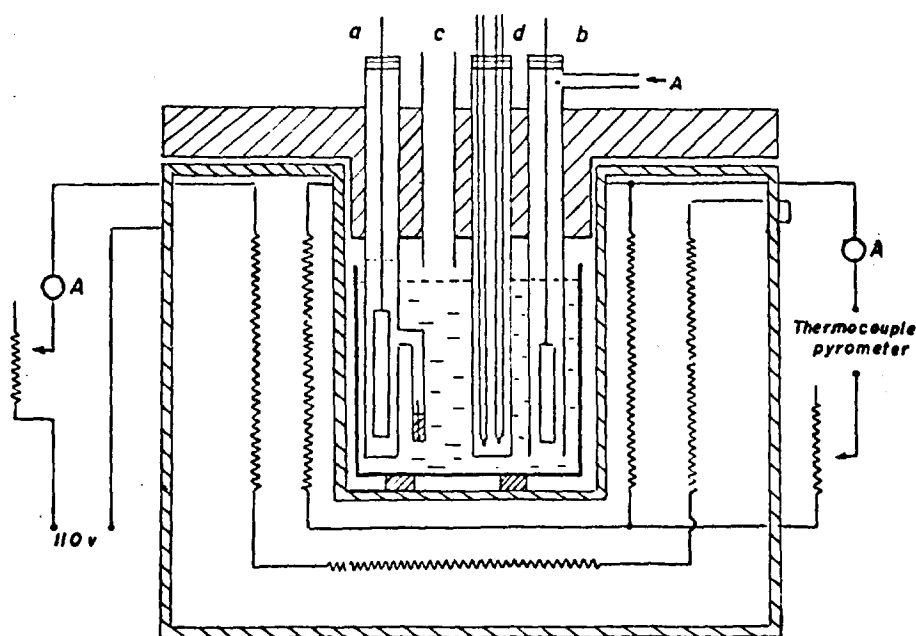

FIG. 1. Apparatus diagram. a—Silver – silver chloride reference electrode. b—Indicator electrode (Ag or Co). c—Feeding tube. d—Temperature control and temperature measuring thermocouples.

argon was preheated and bubbled into the melt through the indicator electrode, both to provide stirring of the solution and to prevent the development of temperature gradients within the melt.

The tubular electric furnace used in these experiments was heavily insulated with successive layers of insulation brick and vermiculite. The furnace was heated by two series of elements. The current through the outer cylindrical elements was regulated by means of a variable transformer. The current through the inner elements was controlled with both a variable transformer and a thermocouple pyrometer controller. This method of heating improved the temperature control within the furnace and increased the

durability of the elements. Temperature control within $\pm 3°$ C. at $1000°$ C. was achieved. The temperature of the melt was measured separately with a calibrated Pt – Pt 13% Rh thermocouple. During the measurements, the reference and indicator electrodes and the two thermocouples (enclosed in silica tubing) were immersed in the melt to ensure that all were at the same temperature.

When not in use, the reference half-cell was cleaned by dipping in pure molten alkali chlorides and was stored at operating temperature inside the furnace. Its potential was checked occasionally against a similar reference electrode which had been freshly prepared.

All potential measurements were made with a Leeds & Northrup Type K potentiometer which, in the range 0–1.6 volts, had a precision of 0.00001 volt.

Results

Solutions of different concentrations of AgCl in the chloride melt solvent were prepared, and the potential of the indicator electrode was measured against the reference at a temperature of $700°$ C. The results of these experiments are shown in Fig. 2 a, from which it is evident that the relationship between $\log(x_2/x_1)$ (where x_1 and x_2 are respectively the mole fractions of AgCl in the reference and indicator electrodes) and the electromotive force is linear, as required from theory. The slope of the line in the figure is 0.192. The slope calculated from the Nernst equation

$$[1] \qquad E_{cell} = (2.303 RT/\mathscr{F})\log(x_2/x_1),$$

where $R = 1.987$ cal. deg.$^{-1}$ mole^{-1},

$\qquad \mathscr{F} = 23,060$ cal./abs. volt gram equivalent,

and $\quad T = 973.2°$ K.,

is 0.193. The excellent agreement between the theoretical and experimental values indicates that there is no change in the activity coefficient for AgCl in this medium for the range of concentrations considered in the experiment, i.e. from 1.10×10^{-3} to 6.35×10^{-2} mole fraction.

The effect of temperature on the electromotive force of a concentration cell was determined for temperatures between $650°$ and $950°$ C., and the results are given in Fig. 2 b. The relationship between temperature and electromotive force is linear with a slope of 3.60×10^{-4} volt/degree, which is in excellent agreement with the theoretical slope of 3.495×10^{-4} volt/degree.

To test the reversibility of the Ag–AgCl electrode, two similar half-cells with different AgCl concentrations were short-circuited for a period of 5 minutes and their potentials then measured against a third reference. The observed changes in potential before and after short-circuiting were of the order of 0.5–1 mv., which could be attributed to temperature gradients within the cells or to small changes in concentration during the short-circuiting. This is in good agreement with the results obtained by Senderoff and Brenner in a similar test of their reference electrode (14).

To study the possible formation of complexes between silver chloride and the alkali chloride melt solvent, the electromotive force of a concentration cell in which the reference electrode contained only pure molten silver chloride was measured.

Ag	AgCl (x)		Asbestos fiber ‖	AgCl	Ag
(−)	KCl–NaCl (1/1 mole)				(+)
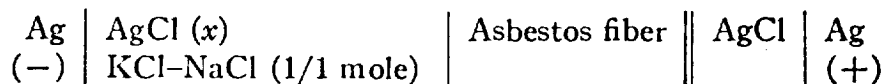
The electromotive force of this cell should be a function of both the individual electrode potentials (E_e) and the liquid junction potential (E_L),
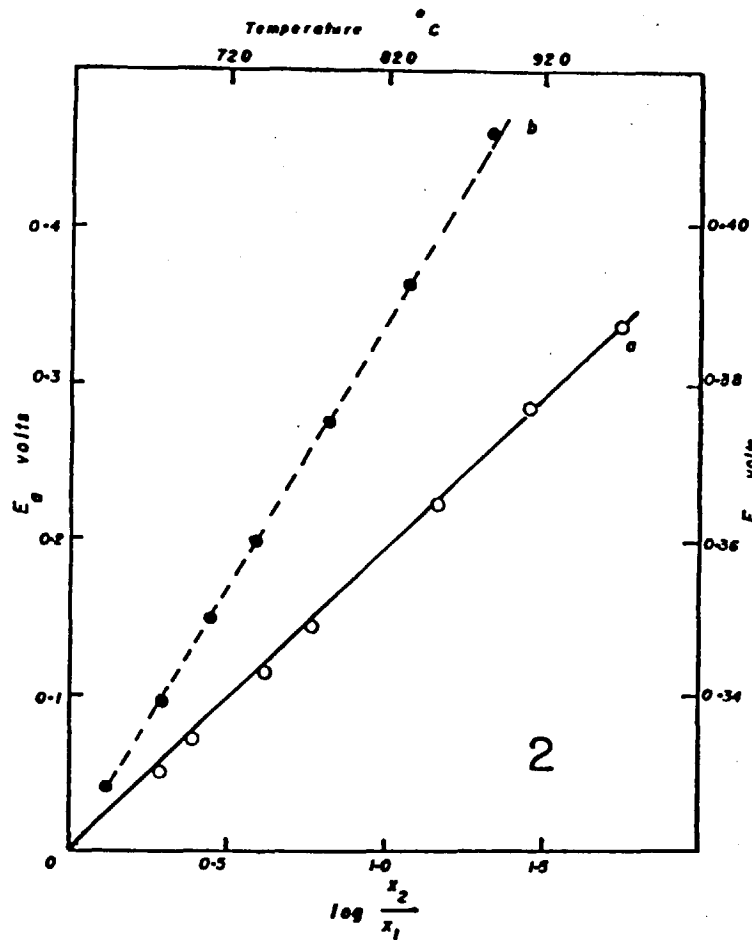
$$[2] \qquad E_{cell} = E_e + E_L.$$

FIG. 2. a—Electromotive forces (E_a) of a silver – silver chloride concentration cell as a logarithmic function of silver chloride concentrations at a constant temperature of 700° C. The mole fraction of silver chloride in the reference electrode is 1.10×10^{-2}.

b—Electromotive forces (E_b) of the same cell as above as a function of temperature at constant silver chloride concentrations ($x_1 = 1.10 \times 10^{-2}$ and $x_2 = 6.35 \times 10^{-2}$ mole fraction).
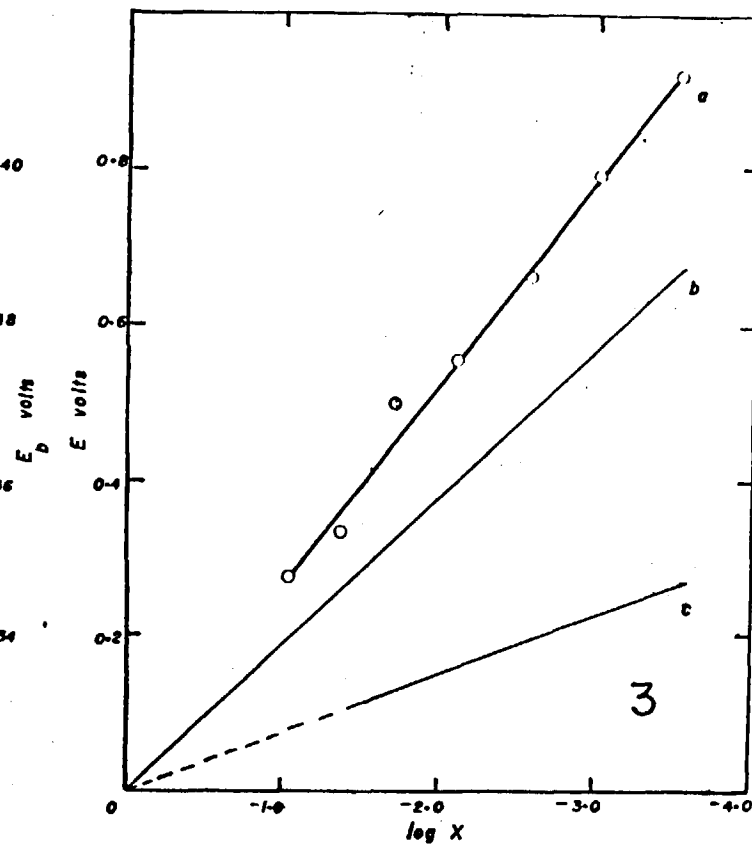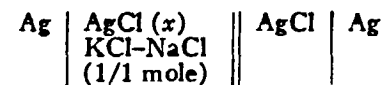
FIG. 3. Electromotive forces of the cell:

$$\text{Ag} \left| \begin{array}{c} \text{AgCl } (x) \\ \text{KCl–NaCl} \\ (1/1 \text{ mole}) \end{array} \right\| \text{AgCl} \left| \text{Ag} \right.$$

as a logarithmic function of silver chloride concentration. a—Experimental results. b—Calculated values. c—Liquid junction potentials (a–b).

In the case of complex formation, where K is the dissociation constant of the complex $AgCl_n^{(n-1)-}$ the electrode potential is given by the equation

[3] $E_e = (2.303RT/\mathscr{F})\log(1/x) + (2.303RT/\mathscr{F})\log(f_s/Kf_c)$,

where f_s and f_c are respectively the activity coefficients of the simple and complex ions. The liquid junction potential is given by an equation of the general form (6)

[4] $$E_L = \frac{-2.303RT}{\mathscr{F}} \int_{c_1}^{c_2} \sum_i t_i \, d\log(x_i f_i),$$

where x_i is the mole fraction of the ith molecular species,

      f_i is the corresponding activity coefficient,

and t_i is the transference number.

By a combination of equations [2], [3], and [4], an expression of the following form is obtained:

[5]
$$\left[E_{cell} - \frac{2.303RT}{\mathscr{F}} \log \frac{1}{x} \right] = \frac{-2.303RT}{\mathscr{F}} \int_{c_1}^{c_2} \sum_i t_i \, d\log x_i$$

$$- \frac{2.303RT}{\mathscr{F}} \left[\int_{c_1}^{c_2} \sum_i t_i \, d\log f_i - \log \frac{f_s}{Kf_c} \right].$$

Since this equation is linear with respect to $[E_{cell} - (2.303RT/\mathscr{F})\log(1/x)]$ and $\log x$, it follows that a plot of these quantities should be a straight line with an intercept equal to the second parenthetical term of equation [5].

Experimental results plotted in Fig. 3 c show that this relationship is linear, as expected. However, when the straight line is extrapolated to unity mole fraction (log = 0), it passes through the origin, thus indicating that no complex is formed between the AgCl and the solvent. Based on this observation, the activity coefficient of AgCl in the melt for this range of concentrations can then be considered as unity. From equation [5], it is seen that the slope of the straight line is a function of several factors which are at present unknown and could not be resolved in the present investigation.
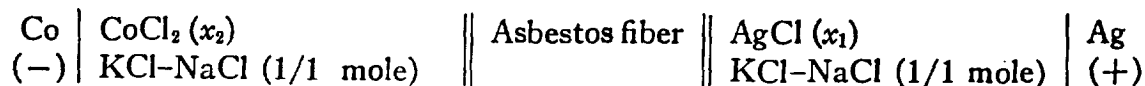
From Fig. 3 c, it is possible to derive an empirical relationship for the potential of a reference half-cell using AgCl diluted with KCl-NaCl, against a reference using pure AgCl at 700° C.:

[6] $E_L = 0.075 \log x$.

From the experimental results above, it follows that the Ag|AgCl electrode, as constructed, is both reversible and thermodynamically predictable. The absence of complex formation between AgCl and the solvent indicates that it can be used to study the formation of other complexes in melts.

B. ELECTROMOTIVE FORCE MEASUREMENTS ON A SILVER–SILVER CHLORIDE, COBALT–COBALTOUS CHLORIDE VOLTAIC CELL

Having established the reversibility and reproducibility of the silver–silver chloride reference electrode, the electromotive force of the following voltaic cell was measured as a function of cobaltous chloride concentration and temperature:

| Co | CoCl$_2$ (x_2) | | Asbestos fiber | | AgCl (x_1) | | Ag |
| (−) | KCl–NaCl (1/1 mole) | ‖ | | ‖ | KCl-NaCl (1/1 mole) | | (+) |

The half-cell to the right is the reference electrode, the half-cell to the left is the indicator electrode, and x_1 and x_2 are respectively the mole fractions of silver chloride and cobaltous chloride in the two solutions. Voltaic cells of this type are practically free of liquid junction potential, owing to the presence of a great excess of the same melt solvent on both sides of the junction.

The design of the indicator electrode was similar to that described for silver in section A. A clean block of cobalt metal (99.9% pure), connected to a platinum wire lead, was inserted in the silica tubing of the indicator half-cell. The electrode was immersed in the molten electrolyte in the cell under a protective stream of oxygen-free argon; when electromotive force measurements were to be made the argon flow was interrupted, because the voltages were unsteady when the gas was bubbling through the electrolyte.

Results

The electromotive force of the silver – silver chloride, cobalt – cobaltous chloride voltaic cell was measured at 710° C. at different cobaltous chloride concentrations. Anhydrous cobaltous chloride was pelletized and added as required to the melt in the cell through a silica feeding pipe leading over the surface of the melt. The results of these measurements are shown in Table I.

TABLE I

ELECTROMOTIVE FORCES OF A COBALT–SILVER VOLTAIC CELL
AS A FUNCTION OF COBALTOUS CHLORIDE CONCENTRATION

Mole fraction of AgCl (x_1)	Mole fraction of CoCl (x_2)	E_{cell} (volts)
6.103×10^{-2}	7.60×10^{-4}	0.3935
6.103×10^{-2}	1.80×10^{-3}	0.3560
6.103×10^{-2}	3.90×10^{-3}	0.3242
6.103×10^{-2}	8.40×10^{-3}	0.2894
6.103×10^{-2}	2.05×10^{-2}	0.2511
6.103×10^{-2}	3.97×10^{-2}	0.2206
6.103×10^{-2}	5.07×10^{-2}	0.2054
6.103×10^{-2}	6.12×10^{-2}	0.1950

The over-all cell reaction in an ideal solution would be

$$Co + 2AgCl \rightleftharpoons CoCl_2 + 2Ag$$

and the cell voltage can be expressed by the Nernst equation in the form:

[7] $$E_{cell} = (E°_{Co} - E°_{Ag}) - (2.303RT/2\mathscr{F})\log(x_2/x_1^2),$$

where $E°_{Co}$ and $E°_{Ag}$ are respectively the standard electrode potentials of the half-cells Co| CoCl$_2$ and Ag | AgCl, under the conditions of the experiment.

From equation [7], it follows that the relationship between E_{cell} and $\log(x_2/x_1)$ should be linear, and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{cell} = E°_{Co} - E°_{Ag}.$$

When the electromotive force of the cell is plotted against $\log(x_2/x_1^2)$, as calculated from the experimental data given in Table I, the results can be represented by a straight line which deviates from linearity at values higher than 4×10^{-2} mole fraction of CoCl$_2$. This is shown in Fig. 4, from which it is found that

$$E°_{Co} - E°_{Ag} = 0.324 \text{ volt.}$$

The accuracy of this value is difficult to establish, but in duplicate experiments it was observed that the value could be reproduced within 0.002 volt. The slope of the linear part of the plot is 0.103 volt, which agrees well with 0.0975 volt calculated from equation [7] for a two-electron electrode process.

The major part of the curve, which is linear, indicates that the activity coefficient of $CoCl_2$ is essentially constant, although small deviations occur at higher mole fractions.

The effect of temperature change on the electromotive force of this voltaic cell was also investigated. The results of these measurements for a temperature range between 650° and 850° C. are shown in Table II.

TABLE II

THE EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELL Co | $CoCl_2$ in KCl–NaCl || AgCl in KCl–NaCl | Ag, for AgCl and $CoCl_2$ mole fractions of 6.10×10^{-2} and 6.12×10^{-2}, respectively

T, ° K.	E_{cell}, experimental (volts)	$E°_{Co} - E°_{Ag}$, calculated (volts)
On heating		
925	0.2194	0.3309
947	0.2100	0.3243
949	0.2113	0.3262
983	0.1950	0.3129
1003	0.1873	0.3083
1028	0.1797	0.3037
1049	0.1732	0.2996
1070	0.1669	0.2958
1097	0.1543	0.2912
1119	0.1540	0.2884
On cooling		
1090	0.1668	0.2981
1081	0.1688	0.2989
1050	0.1792	0.3057
1012	0.1910	0.3126
984	0.1983	0.3170
961	0.2008	0.3169

Included in the table are $E°_{Co} - E°_{Ag}$ values calculated from the experimental results using equation [7]. From these data, using the equations

[8] $$\Delta F° = -nE°\mathscr{F},$$

[9] $$\Delta F° = -2.303\,RT \log K$$

it was possible to calculate, for various temperatures, the effective equilibrium constant for the reaction

$$Co + 2AgCl \rightarrow CoCl_2 + 2Ag.$$
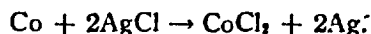
This equilibrium constant is understood to include any effects on the reaction due to the presence of the melt solvent. The results of these calculations are shown in Fig. 5, where $\log K$ is plotted against the reciprocal of the absolute temperature. It is seen that the curve is linear over this temperature range, i.e. 650° to 850° C. In Fig. 5, the best straight line was calculated from the experimental results applying the least squares method. The average deviation of $\log K$ from the experimental values is only ± 0.027.

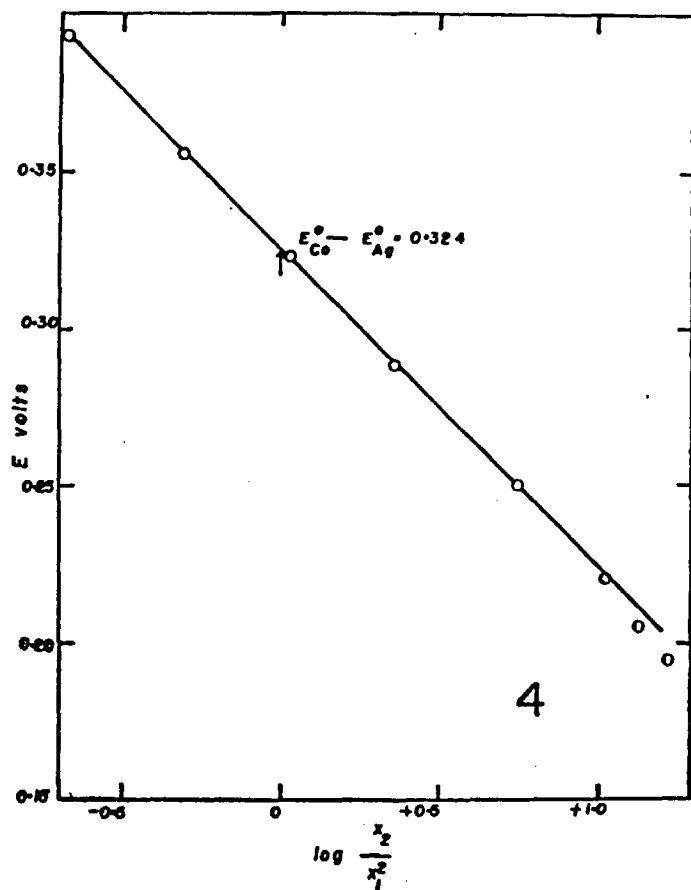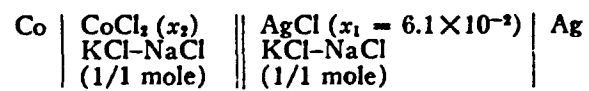The heat of the reaction taking place in the cell, which is the difference between the

FIG. 4. Electromotive forces of the cell:

Co | CoCl$_2$ (x_2) | | AgCl (x_1 = 6.1×10^{-2}) | Ag
     | KCl–NaCl | | KCl–NaCl
     | (1/1 mole) | | (1/1 mole)

as a function of log (x_2/x_1^2), at a constant temperature of 710° C.
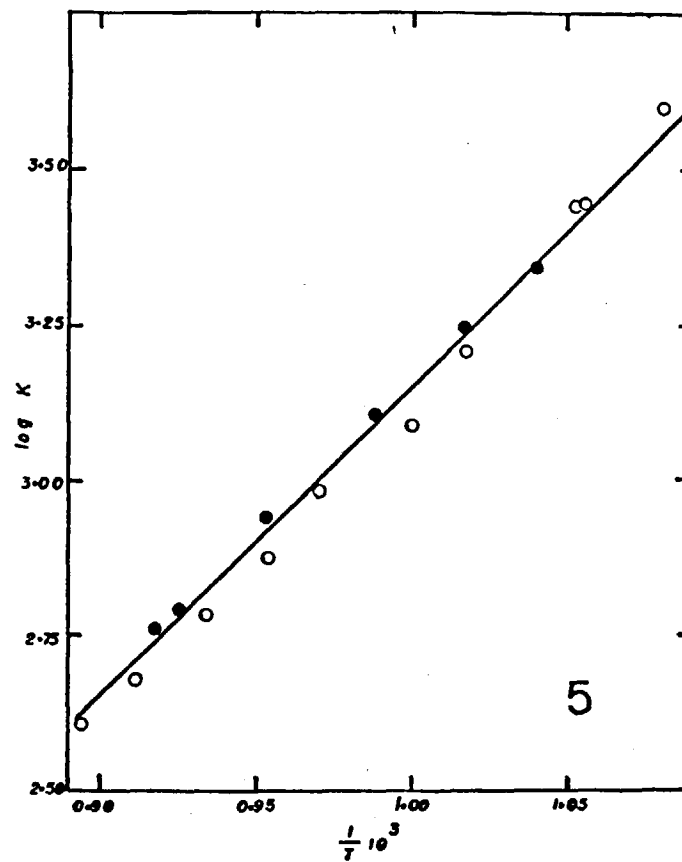
FIG. 5. The variation of log K with the reciprocal of temperature for the system:

Co | CoCl$_2$ (x_2 = 6.12×10^{-2}) | | AgCl (x_1 = 6.10×10^{-2}) | Ag
     | KCl–NaCl (1/1 mole) | | KCl–NaCl (1/1 mole) |
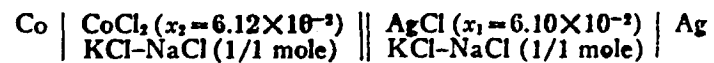
O With increasing temperature.   ● With decreasing temperature.

FLENGAS AND INGRAHAM: VOLTAIC CELLS, I

1147

heats of formation of cobaltous chloride and silver chloride in the melt, can be calculated with the aid of the van't Hoff equation,

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

The heat of reaction thus obtained from the slope of the straight line in Fig. 5 is:

$$\Delta H_r = -22.8 \pm 1.3 \text{ kcal.}$$

DISCUSSION

In the foregoing experimental work, a standard electrode potential for cobalt was calculated for the conditions of the experiments. The exact thermodynamic significance of this potential will now be discussed.

By definition, the standard electrode potential of a voltaic cell is given by the algebraic sum of the standard single electrode potentials of the two constituent half-cells. This in turn is defined as the potential of the electrode when the species involved in the electrode process are at unit activity.

When dealing with molten salt solutions, it will be realized that the fundamental method of expressing concentrations is by mole fractions. This implies that a mole fraction of unity represents the pure solute without solvent. Thus, in the case of the Co–Ag voltaic cell, the standard electrode potential is defined as the electromotive force of the cell

$$\text{Co} \mid \text{CoCl}_2 \ (x_2 = 1) \ \| \ \text{AgCl} \ (x_1 = 1) \mid \text{Ag.}$$

Because of the unknown boundary potential, the experimentally measured electromotive force would not represent the standard electrode potential. However, the standard potential can be calculated from the theoretical data of Hamer, Malmberg, and Rubin (7), as

$$E^{\circ}_{\text{Co}} - E^{\circ}_{\text{Ag}} = 0.193 \text{ volt at } 710^{\circ} \text{ C.}$$

A comparison of the theoretical value calculated above with that obtained in these experiments (0.324 volt) is of interest because of the indicated lack of ideality in molten salt solutions. Since the AgCl–KCl–NaCl system was shown earlier in this paper to be ideal, the deviation must be attributed to a non-ideality in the CoCl_2–KCl–NaCl system, and may represent either a difference in activity or a tendency to complex formation with the solvent, or both. From available data, these effects cannot be differentiated and, in any case, they could be expressed entirely as a complexing tendency.

On the assumption of complex formation, it is possible to calculate the dissociation constant of the cobaltous chloride complex ion in the molten alkali chloride solvent by application of equations [8] and [9]. In this calculation, E° of equation [8] was replaced by the difference between the experimental and theoretical standard electrode potentials. This difference is -0.131 volt, and the resulting dissociation constant is 4.5×10^{-2}, which indicates a weak complex.

REFERENCES

1. BLICKSLAYER, H. J. Rec. trav. chim. 46, 305 (1927).
2. BOCKRIS, J. O'M., HILLS, G., INMAN, D., and YOUNG, L.   J. Sci. Instr. 33, 438 (1956).
3. DELIMARSKI, YU. Zhur. Obshcheĭ Khim. 26, 2968 (1956).
4. DELIMARSKI, YU. Zhur. Fiz. Khim. 29, 28 (1955).
5. FLENGAS, S. and RIDEAL, E. Proc. Roy. Soc. A, 233, 443 (1956).
6. GLASSTONE, S. Introduction to electrochemistry. D. Van Nostrand Company, Inc., New York. 1951. p. 211.
7. HAMER, W., MALMBERG, M., and RUBIN, B. J. Electrochem. Soc. 103, 8 (1956).

8. LEWIS, G.   Z. Phys. Chem. 52, 310 (1905).
9. LORENZ, R. and KAUFLER, F.   Die Elektrolyse Geschmolzener Selze. Verlag von Johann Ambrosius
      Bartz, Leipzig. 1909.
10. SALSTROM, E. and HILDEBRAND, J.   J. Am. Chem. Soc. 52, 4641 (1930).
11. SALSTROM, E.   J. Am. Chem. Soc. 53, 1794 (1931).
12. SALSTROM, E. and HILDEBRAND, J.   J. Am. Chem. Soc. 54, 4257 (1932).
13. SALSTROM, E., KEW, T., and POWELL, T.   J. Am. Chem. Soc. 58, 1848 (1936).
14. SENDEROFF, S. and BRENNER, A.   J. Electrochem. Soc. 101, 31 (1954).
15. VERDIECK, R. and Yntenia, L.   J. Phys. Chem. 46, 344 (1942).
16. WACHTER, A. and HILDEBRAND, J.   J. Am. Chem. Soc. 52, 4655 (1930).