Equilibrium was obtained in 14 to 84 days. The results are listed in Table I and plotted, together with data for the system NH_3–H_3PO_4–H_2O (*1, 2, 4*), in Figure 1. Over the pH range 4 to 8, the saturating phases at 0° C. are $(NH_4)_2 \cdot H_2P_2O_7$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_4P_2O_7 \cdot H_2O$. These three compounds and $(NH_4)_4P_2O_7$ are the saturating phases at 25° C. Both invariant points at 0° C. were determined. Two of the three invariant points at 25° C. were determined; the third, representing the solution saturated with $(NH_4)_2 \cdot H_2P_2O_7$ and $(NH_4)_3HP_2O_7 \cdot H_2O$, was estimated to contain 11.5% N and 44% P_2O_5 and to have a pH of 4.7.

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Thermodynamic Properties of Molten Solutions of $MgCl_2$–KCl, $MgCl_2$–NaCl, and $MgCl_2$–KCl–NaCl

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Thermodynamic properties of molten magnesium chloride–alkali metal chloride solutions have been evaluated from e.m.f. data obtained with galvanic cells of the type

$$MgBi(l)\,|\,MgCl_2(N_1)MCl(N_2)(l)\,|\,\text{graphite},\ Cl_2(g)$$

where MCl represents the alkali metal chloride. Excess functions have been calculated for $MgCl_2$–KCl and $MgCl_2$–KCl–NaCl systems at 800° C. and for the $MgCl_2$–NaCl system at 825° C. The experimental values obtained for the excess partial molar free energy of $MgCl_2$ in these solutions have been compared with values calculated on the basis of the Temkin theory of molten salts. For the calculation, a model involving the existence of the complex ion $MgCl_4^{-2}$ was assumed. The agreement between experimental and calculated values is taken as evidence that the model can be used to interpret the systems studied.

THE thermodynamic properties of molten salt solutions are often indicative of strong deviations from ideality which are generally attributed to chemical interaction of the components to form relatively stable complex ions. The investigation reported in this paper consists of an evaluation and an interpretation of the thermodynamic properties of melts containing magnesium chloride and alkali metal chlorides.

Various experimental methods have been used by other workers to study the properties of chloride melts containing $MgCl_2$. These include measurement of density (*5. 16*), electrical conductivity (*2, 4, 16, 18, 26*), viscosity (*3*), surface tension (*8*), transference number (*1*), electromotive force (*22, 23*), and vapor pressure (*24*).

Many of the studies have provided evidence of the existence of mixed compounds and complex ions of magnesium. For example, the phase diagram of the $MgCl_2$–KCl system has been interpreted in terms of the formation of the solid compounds $MgCl_2$–KCl and $MgCl_2$–2KCl (*17, 19*), and the phase diagram of the $MgCl_2$–NaCl system has been similarly interpreted in terms of the compounds $MgCl_2$–NaCl and $MgCl_2$–2NaCl (*20*). Flood and coworkers (*11-13*) interpreted the shape of the liquidus curve in the phase diagram of the $MgCl_2$–KCl system as indicating the presence of the $MgCl_4^{-2}$ ion in the liquid phase. Flood and Urnes (*14*) propose that the compound $KMgCl_3$ undergoes the following dissociation on melting:

$$2KMgCl_3 \rightleftarrows 2K^+ + Mg^{+2} + MgCl_4^{-2} + 2Cl^-.$$

Other reported work relative to the solution thermodynamics of melts containing $MgCl_2$ includes a study (*29*) of the equilibrium:

$$MgCl_2(l) + \tfrac{1}{2}\,O_2(g) \rightleftarrows MgO(s) + \tfrac{1}{2}\,Cl_2(g).$$

In the investigation reported in this paper, electrochemical cells of the type

$$MgBi(l)\,|\,MgCl_2(N_1)MCl(N_2)(l)\,|\,\text{graphite},\ Cl_2(g)$$

were employed. For comparison, the cells used by Markov (*22, 23*) were of two types, namely,

$$Mg\,|\,MgCl_2\text{–}KCl\ \text{eut.}\,|\,\text{porcelain powder membrane}\,|\,MgCl_2(N_1)KCl(N_2\,|\,Mg$$

and

$$Mg(l)\,|\,MgCl_2\text{–}KCl(l)\,|\,\text{graphite},\ Cl_2(g).$$

The results obtained by Markov from the two cells were not in good agreement.

The use of galvanic cells for the study of high temperature molten chloride solutions is often limited by the solubility of metals in their molten chlorides. Metal-metal halide solubility has been investigated rather extensively by

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Bredig and coworkers (*6, 7*), for example. As in the investigation reported here, other attempts have been made to circumvent this difficulty by the use of an alloy electrode. Smirnov and Ivanovskii (*27*) investigated the thermodynamic properties of the system $ThCl_4$ in LiCl–KCl eutectic by use of a galvanic cell containing a liquid Th-Zn electrode. Similarly, a Ce-Sn electrode was used by Senderoff, Mellors, and Bretz (*25*) to study the $CeCl_3$–KCl system. Both of these studies utilized an electrode in which a solid alloy phase was in equilibrium with the liquid. The exact composition of the electrode material was not determined. In this study, however, a liquid phase alloy system was used. The alloy was analyzed and appropriate thermodynamic corrections were applied in the calculation of the free energy values for the salts.

EXPERIMENTAL

A galvanic cell was constructed using a chlorine electrode and a bismuth-magnesium alloy electrode. The chlorine electrode consisted of a graphite rod (⅜-inch. o.d. and 1½-inches long) having a ¼-inch hole drilled along its length to allow passage of the chlorine. A ⅛-inch threaded graphite rod was used in establishing electrical contact with the electrode, which was supported vertically by a quartz tube through which the chlorine passed. This assembly was enclosed in a separate Vycor tube to prevent the chlorine from contacting other parts of the cell. The bottom of the tube was closed with two fritted quartz disks through which salt solution within the assembly could make contact with the rest of the cell. The bismuth-magnesium alloy was contained in a graphite cup which was attached to a movable graphite rod to facilitate its introduction into and removal from the molten salt solution. The latter was contained in a Vycor cup within the Vycor cell (2½-inch o.d.).

Anhydrous magnesium chloride, obtained from the Carborundum Company, was found to contain ~0.01% Fe, ~0.001% Ca, ~0.001-0.01% Cu, and ~0.001% Zr by spectrographic analysis. Prior to use in the galvanic cell, adsorbed water was removed by slowly heating the salt in a stream of dry hydrogen chloride gas. The salt was fused, and then hydrogen chloride was bubbled through the liquid. Finally, the vessel was purged with helium which had been previously dried over titanium chips at 800° C. After filtration through a quartz fritted disk, the salt was cooled in an helium atmosphere. Analysis of the purified material gave Cl/Mg = 2.005 and a maximum MgO content of 0.06%. Reagent grade KCl and NaCl were dried in a similar manner except that they were not fused.

In the preparation of salt mixtures, the dried salts were mixed in the desired proportions and fused under vacuum in a Vycor filter apparatus. After fusion, helium pressure was applied, and the liquid was forced through a quartz frit into a quartz tube. The salt mixture was then allowed to cool under a helium atmosphere, and the salt slug was sealed off in this quartz tube.

The bismuth (obtained from the Cerro de Pasco Co.) used for the alloy electrode was first filtered in vacuo and cast into small ingots. These were placed with the proper amount of magnesium in the graphite crucible and fused in an helium atmosphere. The magnesium was spectroscopic grade magnesium purchased from Johnson, Matthey and Co., Ltd.

In a typical experiment, the purified salt slug was introduced into the assembled cell, and the cell was evacuated. The cell was heated slowly until the salt charge had melted. The alloy electrode was then lowered into the melt, and dry chlorine was allowed to pass slowly through the chlorine electrode.

The temperature of the cell was measured by a calibrated Chromel-Alumel thermocouple, supported in a quartz tube and placed in the melt between the two electrodes. The temperature of the furnace could be controlled to ±1° C. by use of a Minneapolis-Honeywell Pyrovane controller.

The thermo-e.m.f. of the cell was measured, after short-circuiting the electrodes with a graphite rod, over a temperature range, and appropriate corrections were applied to the galvanic cell readings. A correction to standard conditions was also made for the pressure of the chlorine gas. To check the operation of the chlorine electrode and the corrections for the thermo-e.m.f. and chlorine gas pressure, the potential of the cell

$$Pb(l) \mid PbCl_2(l) \mid \text{graphite}, Cl_2(g)$$

was measured. The results were in excellent agreement with values tabulated by Hamer, Malmberg, and Rubin (*15*).

The e.m.f. of the cell was measured at constant temperature by means of Rubicon precision potentiometer, until a constant value was obtained for several readings over a 15-minute period. The temperature of the cell was then changed, and the e.m.f. measuring sequence was repeated. For a cell having a given composition, the temperature was changed in a random manner. No hysteresis was detected. Cell potential readings were reproducible to ±1 millivolt at any given temperature.

At the end of a run, a sample of the liquid was withdrawn from the melt. The alloy electrode was then cleaned of any adhering salt, and the metal slug was dissolved in 50% nitric acid and submitted for magnesium analysis. The bismuth was precipitated as the sulfide with thioacetamide. After two precipitations, the filtrate was bismuth free. Titan yellow was added to the solution, and magnesium was determined spectrophotometrically. The salt sample was dissolved in 2% hydrochloric acid, and magnesium was determined by titration with EDTA using Eriochrome Black T as indicator.

RESULTS AND DISCUSSION

The salt mixtures studied were $MgCl_2$–KCl, $MgCl_2$–NaCl, and $MgCl_2$–(NaCl-KCl, eut.). For the latter, the molar ratio of NaCl to KCl was 1.043. The over-all cell reaction can be written as

$$MgBi(l) + Cl_2(g) = MgCl_2(MCl)(l).$$

The cells are of the type:

$$MgBi(l) \mid MgCl_2\,(N_1)\ MCl\,(N_2)\ (l) \mid \text{graphite}, Cl_2\,(g).$$

E.m.f. values in volts are given over a temperature range for cells having a MgBi (l) electrode composition expressed as mole fraction of Mg and a molten salt solution composition expressed as mole fraction of $MgCl_2$. These values have been tabulated and deposited with the A.D.I.

Conversion of the free energy change for this reaction to that for the reaction of interest, namely,

$$Mg(l) + Cl_2(g) = MgCl_2(MCl)\ (l)$$

requires a knowledge of the excess partial molar free energy and excess partial molar entropy of magnesium in the alloy. Such data have been published by Egan (*9*). Data for the heat and the entropy of fusion and the heat capacities of solid and liquid magnesium were taken from the compilation of Kubaschewski and Evans (*21*). The activity of $MgCl_2$ in the melt is obtained from the partial molar free energy of $MgCl_2$ in the melt and the molar free energy of pure $MgCl_2$ by means of the equation

$$F_{MgCl_2} - F^0_{MgCl_2} = RT \ln a_{MgCl_2}.$$

The excess partial molar free energy, the activity coefficient, and the mole fraction of $MgCl_2$ are then related by

$$F^E_{MgCl_2} = F_{MgCl_2} - F^0_{MgCl_2} - RT \ln N_{MgCl_2} = RT \ln \gamma_{MgCl_2}.$$

Values of $F^E_{MgCl_2}$ and γ_{MgCl_2} are given in Table I for three series of melts differing in the kind of alkali metal chloride present. The variation of $F^E_{MgCl_2}$ with composition is illustrated in Figure 1.

Table I. Excess Partial Molar Free Energy and Activity Coefficient of MgCl₂ in Three Systems

N_{MgCl_2}	$-F^E_{MgCl_2}$ Kcal. Mole^{-1}	γ_{MgCl_2}
	$MgCl_2$–KCl at 800° C.	
1.000	0	1.00
0.792	0.5	0.79
0.710	0.9	0.66
0.563	2.7	0.29
0.469	4.4	0.13
0.398	5.2	0.09
0.343	5.7	0.073
0.325	6.2	0.057
0.252	9.8	0.011
0.168	11.2	0.0056
0.088	11.6	0.0046
0.020	11.8	0.0042
0.015	11.5	0.0048
	$MgCl_2$–NaCl at 825° C.	
1.00	0	1.00
0.744	0	1.00
0.647	0.7	0.72
0.533	1.3	0.55
0.438	2.4	0.33
0.359	3.5	0.22
0.325	3.7	0.18
0.281	4.2	0.15
0.189	6.0	0.064
0.092	7.2	0.037
0.025	7.1	0.038
	$MgCl_2$ (NaCl–KCl) at 800° C.	
1.000	0	1.00
0.791	0	1.00
0.640	1.1	0.60
0.568	2.2	0.36
0.478	2.6	0.30
0.410	3.3	0.22
0.293	6.1	0.061
0.227	7.5	0.032
0.089	10.3	0.089
0.054	10.3	0.089
0.009	10.5	0.081

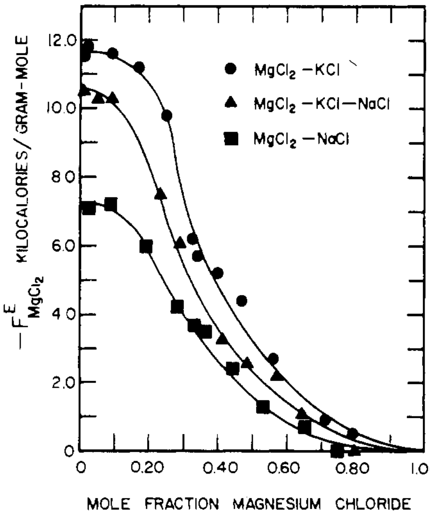

Figure 1. Excess partial molar free energy of MgCl₂ in alkali chloride melts

MgCl₂–KCl at 800° C., MgCl₂–KCl–NaCl at 800° C., MgCl₂–NaCl at 825° C.

The excess partial molar free energies of KCl and of NaCl in the binary systems were calculated by means of the Gibbs-Duhem relationship, e.g.,

$$F^E_{KCl} = \int_0^{N_{MgCl_2}} \frac{F^E_{MgCl_2}}{N^2_{KCl}}\, dN_{MgCl_2} - \frac{N_{MgCl_2} F^E_{MgCl_2}}{N_{KCl}}.$$

The integral was evaluated numerically by use of Weddle's rule. Values of the excess partial molar free energy for KCl and NaCl and of the total excess free energy are given in Table II. The results for NaCl compare favorably with those obtained directly from e.m.f. measurements at 820° C. by Egan and Bracker (*10*).

Large negative values of $F^E_{MgCl_2}$ in the melt are attributed to the formation of the complex ion $MgCl_4^{-2}$. As previously mentioned, various other experimental measurements of the physical properties of magnesium chloride melts have led the investigators to postulate the existence of this complex species. If it is assumed that the melt is, to a first approximation, an ideal solution of K^+, Mg^{+2}, $MgCl_4^{-2}$ and Cl^- ions, then, on the basis of the Temkin (*28*) theory of ionic melts, the relative partial molar free energy of $MgCl_2$ can be written as

Table II. Excess Free Energy Functions

	$MgCl_2$–KCl, t = 800° C.		$MgCl_2$–NaCl, t = 825° C.	
N_{MgCl_2}	$-F^E_{KCl}$ Kcal. mole^{-1}	$-F^E$ Kcal. mole^{-1}	$-F^E_{NaCl}$ Kcal. mole^{-1}	$-F^E$ Kcal. mole^{-1}
0.1	0	1.1	0.2	0.9
0.2	0.6	2.3	0.6	1.2
0.3	1.5	3.2	1.1	1.9
0.4	2.7	3.5	1.8	2.3
0.5	4.2	3.6	2.5	2.2
0.6	5.7	3.3	3.3	1.9
0.7	7.3	2.9	4.1	1.4
0.8	8.6	2.2	5.0	1.2
0.9	9.8	1.2	5.9	0.7

$$F^M_{MgCl_2} = RT \ln N_{Mg^{+2}} N^2_{Cl^-},$$

where

$$N_{Mg^{+2}} = \frac{n_{Mg^{+2}}}{n_{Mg^{+2}} + n_{K^+}}$$

and

$$N_{Cl^-} = \frac{n_{Cl^-}}{n_{Cl^-} + n_{MgCl_4^{-2}}},$$

where *n* is the number of moles of the indicated ion present. The existence of the equilibrium

$$MgCl_4^{-2} \rightleftarrows Mg^{+2} + 4Cl^-$$

will clearly have most effect on the thermodynamic properties of the melts in the region $N_{MgCl_2} < 0.33$, since above that concentration there is not enough chloride present to complex all the magnesium. The equilibrium constant *K*, as defined by the expression

$$K = \frac{N_{Mg^{+2}} N^4_{Cl^-}}{N_{MgCl_4^{-2}}}$$

was therefore calculated from the relative partial molar free energy of $MgCl_2$ at the point N_{MgCl_2} = 0.20. At this point, *K* was found to be 1.8 × 10^{-3} in the $MgCl_2$–KCl melt at 800° C. and 2.3 × 10^{-2} in the $MgCl_2$–NaCl system at 825° C. By using these values and the expression for the mole fraction of Mg^{+2} and Cl^-, the value of the relative partial molar free energy of $MgCl_2$ was calculated at various compositions from the Temkin model for the melts. The results of this calculation are illustrated in Figure 2.

Values for the dissociation constant were also calculated by another method based on extrapolation, from dilute solution to $N_{MgCl_2} = 1$, of a plot of F_{MgCl_2} as a function of log N_{MgCl_2} (Figure 3). The extrapolated value, $F^*_{MgCl_2}$, is related to the equilibrium constant by the equation

$$F^0_{MgCl_2} - F^*_{MgCl_2} = -RT \ln K.$$

In each case, the value obtained is the same as that calculated by use of the Temkin theory.

The difference between the values of the excess partial molar free energy of $MgCl_2$ in the binary systems containing KCl and those containing NaCl can be attributed to the greater polarizing power of Na^+ as compared to K^+. Since the ionic radius of Na^+ is 0.95 A., compared with 1.33 A. for K^+, the former will exhibit a greater attraction for chloride ions than the latter. This phenomenon has been observed in other molten salt systems (*6, 7, 11–14, 19, 20, 25, 27, 29*).

The agreement between the observed behavior and that predicated on the basis of the assumed model indicates that the model can be used to interpret the behavior of the molten salt systems studied. The agreement, however, is not in itself proof of the existence of the $MgCl_4^{-2}$ complex ion and other models are not excluded.

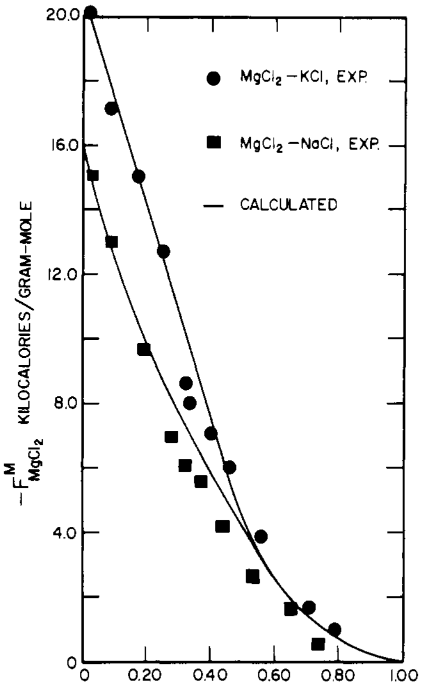

Figure 2. Comparison of experimental and calculated (solid line) relative partial molar free energy of $MgCl_2$ in $MgCl_2$–KCl melts at 800° C. and in $MgCl_2$–NaCl melts at 825° C.

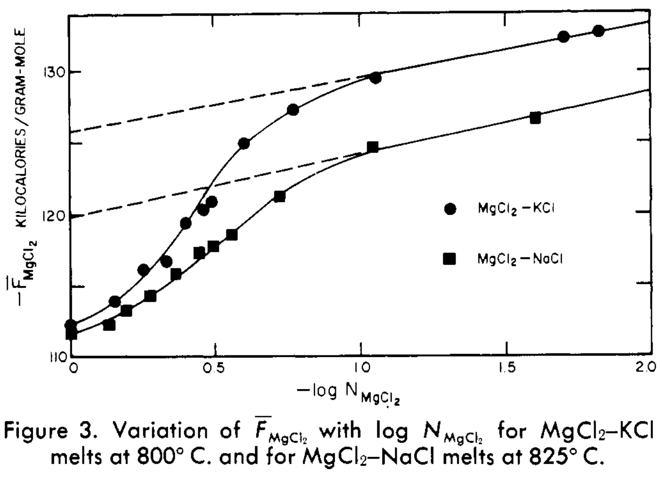

Figure 3. Variation of $\bar{F}_{MgCl_2}$ with log N_{MgCl_2} for $MgCl_2$–KCl melts at 800° C. and for $MgCl_2$–NaCl melts at 825° C.

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