CHEMICAL REVIEWS

MOLTEN SALT ELECTROMOTIVE FORCE FORMATION CELLS

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I. INTRODUCTION

At present, the properties of solid ionic crystals are fairly well understood,[1-3] whereas the insight into the properties of ionic liquids is still limited. This is mainly due to the fact that the long-range order characteristic of solid salts disappears on melting and is replaced by local ordering.[4-6] In addition to such theoretical difficulties, the experimental determination of the properties of molten salts requires special experimental techniques as most molten salts and salt mixtures have high melting points, are corrosive, and are volatile.

Various statistical methods have been developed for the calculation of equilibrium properties of liquids.[7-9] However, only recently have liquid theories been modified for the calculation of equilibrium properties of ionic melts.[4,6,10-15] Unfortunately, reliable experimental data to test these theories are still lacking.

The equilibrium properties of molten salts can be obtained by various experimental techniques, e.g., calorimetric heats of mixing,[6,16,17] vapor pressure

(1) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1962.
(2) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1958.
(3) W. Jost, "Diffusion," Academic Press Inc., New York, N. Y., 1960.
(4) F. H. Stillinger, Jr., in "Molten Salt Chemistry," M. Blander, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1963, p 1.
(5) H. A. Levy and M. D. Danford in ref 4, p 109.
(6) T. Forland in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 63.

(7) J. S. Rowlinson, "Liquids and Liquid Mixtures," Academic Press Inc., New York, N. Y., 1959.
(8) J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.
(9) R. W. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, 1960.
(10) H. Reiss, J. L. Katz, and O. J. Kleppa, *J. Chem. Phys.*, **36**, 144 (1962).
(11) M. Blander, *ibid.*, **34**, 432 (1961); *J. Phys. Chem.*, **63**, 1262 (1959); *J. Chem. Phys.*, **34**, 697 (1961); **36**, 1092 (1962); **37**, 172 (1962).
(12) J. Lumsden, *Discussions Faraday Soc.*, **32**, 138 (1961).
(13) G. E. Blomgren, *Ann. N. Y. Acad. Sci.*, **79**, 781 (1960); *J. Phys. Chem.*, **66**, 1500 (1962).
(14) C. M. Carlson, H. Eyring, and T. Ree, *Proc. Natl. Acad. Sci. U. S.*, **46**, 333 (1960).
(15) R. Vilcu and C. Misdolea, *J. Chem. Phys.*, **45**, 3414 (1966).
(16) M. Blander in ref 4, p 127.
(17) O. J. Kleppa, *Ann. Rev. Phys. Chem.*, **16**, 187 (1965).

measurements,[18] cryometry,[19-21] and the use of electrochemical cells.[6,16,22-24] Apart from high-temperature heats of mixing calorimetry, the measurement of the electromotive force of electrochemical cells is possibly the method capable of greatest precision and accuracy, provided due attention is directed to certain features of the experimental work. The calculation of excess free energies of molten salt mixtures from concentration cell data is well understood,[6,22] but it is difficult to give an exact meaning to the results which have been reported, since the liquid junction potential is generally unknown; this makes the derived thermodynamic results, such as activities, inexact. This uncertainty does not arise in the calculation of the free energies and excess free energies from the emf data of equilibrium-type cells, i.e., cells with two different electrodes.

Although discussions of equilibrium emf data have been a part of previous reviews[6,12,13,16] which encompassed the broad field of solution chemistry of molten salts, a comprehensive and critical review of equilibrium emf data appears to be lacking. The thermodynamics of mixing for molten salts can be derived from equilibrium emf measurements. In this paper, such results are critically reviewed, the scope being restricted to binary molten salt mixtures with a common ion, including charge-symmetrical and charge-unsymmetrical mixtures. For this purpose the original emf data were systematically recalculated to establish comparisons of the free-energy values of various workers that would be significant and also so that the values of different mixtures could be examined and intercompared.

A. SYMBOLS AND TERMINOLOGY

Avogadro constant	N
Faraday constant	F
Temperature in °K	T
Temperature in °C [0°C (ice point) = 273.15°K]	t
Gas constant	R
Thermochemical calorie	cal
Molar Gibbs free energy	G
Excess molar Gibbs free energy	G^E
Molar heat of mixing	H^E

Excess molar entropy of mixing	S^E
Excess chemical potential of component AX; partial excess molar Gibbs free energy of mixing of component AX	μ^E_{AX}
Partial excess heat of mixing of component AX	h^E_{AX}
Partial excess molar entropy of mixing of component AX	s^E_{AX}
Mole fraction of component AX [in a binary mixture AX(x), BX($1-x$), the mole fraction of AX is $N_{AX}/(N_{AX}+N_{BX})$]	x_{AX}
Cell emf	E
Number of equivalents	z
Activity coefficient	f

The activity coefficient (f) and the excess chemical potential (μ^E) are related by the equation

$$\log f = 0.218545 T^{-1}\mu^E$$

(μ^E units, cal/mole).

II. DISCUSSION OF CELLS

The theoretical and practical principles of emf equilibrium cells for use with molten salts have been described recently elsewhere.[6,22-24] These cells consist essentially of two electrodes, each of which is reversible to one ionic constituent of a molten salt or a molten salt mixture.

The various electrodes used in the study of molten salts have been reviewed by Laity[22] and by Alabyshev, Lantratov, and Morachevskii.[24] Two kinds of electrodes can be distinguished: cation metal electrodes such as Ag, Zn, and Pb and anion gas electrodes such as $Cl_2|C$, $Br_2|C$, $I_2|C$, and $NO_2-O_2|Pt$. In addition, cells have been developed in which glass functions as a cation indicator electrode.[25-31] Equilibrium conditions must be maintained for the evaluation of free energies from electrochemical cells. For this condition to be satisfied the electrodes must behave reversibly, and no intervening phenomena such as a high solubility of the metal electrode or the occurrence of mixed potentials must influence the cell emf. Apart from kinetic considerations the reversibility of formation cells may be investigated by comparing the experimental emf between two electrodes in a single molten salt with emf's calculated from thermochemical

(18) H. Bloom, *Pure Appl. Chem.*, **7**, 389 (1963).
(19) G. J. Janz and J. Goodkin, *J. Phys. Chem.*, **64**, 808 (1960); **63**, 1975 (1959).
(20) M. Rolla, P. Franzosini, and R. Riccardi, *Discussions Faraday Soc.*, **32**, 84 (1961).
(21) J. Brynestad, K. Grjotheim, F. Gronvold, J. L. Holm, and S. Urnes, *ibid.*, **32**, 90 (1961).
(22) R. W. Laity in "Reference Electrodes," D. J. G. Ives and G. J. Janz, Ed., Academic Press Inc., New York, N. Y., 1961.
(23) J. K. Delimarsky and B. F. Markov, Ed., "Electrochemistry of Fused Salts," The Sigma Press, Washington, D. C., 1961.
(24) A. F. Alabyshev, M. F. Lantratov, and A. G. Morachevskii, Ed., "Reference Electrodes for Fused Salts," The Sigma Press, Washington, D. C., 1965.

(25) T. Ostvold, "On the Application of Glass Membranes as Alkali Electrodes at Elevated Temperatures," Ph.D. Thesis, Trondheim, Norway, 1966.
(26) T. Forland and T. Ostvold, *Acta Chem. Scand.*, **20**, 2086 (1966).
(27) T. Ostvold, *ibid.*, **20**, 2187, 2320 (1966).
(28) C. G. M. Dijkhuis, "An Investigation of Molten Cadmium Halide-Alkali Halide Mixtures by EMF Measurements," Ph.D. Thesis, University of Amsterdam, The Netherlands, 1964.
(29) C. G. M. Dijkhuis and J. A. A. Ketelaar, *Electrochim. Acta*, **11**, 1607 (1966).
(30) K. Notz and A. G. Keenan, *J. Phys. Chem.*, **70**, 662 (1966).
(31) S. Sternberg and C. Herdlicka, *Rev. Roumaine Chim.*, **11**, 29 (1966).

data.[32-34] There are uncertainties involved in some "theoretical emf's" due to approximations in thermochemical data. However, the emf's of cells with a single salt as molten electrolyte $(E°)$ are of prime importance for the investigation of the mixtures. A comparison between experimental emf's and thermochemical emf's has therefore been presented in Tables I and II. For some cells these tables show excellent

TABLE I

$E°$ VALUES (mV) OF FORMATION CELLS WITH CHLORIDES AS LIQUID ELECTROLYTE AT VARIOUS TEMPERATURES (°C) AS CALCULATED FROM LITERATURE SOURCES BY MEANS OF A LINEAR AND A QUADRATIC LEAST-SQUARES ANALYSIS

a. Ag|AgCl|Cl₂|C

500°	600°	700°	800°	900°	Ref
895.0	868.4	842.1	815.8	789.5	35
898.3	869.0	841.1	814.7	789.8	37
893.9	864.5	838.5	816.0	796.5	38
890.9	863.4	835.9	808.3	780.7	39
899.7	871.1	842.5	814.0	785.4	42
898.8	865.8	832.7	799.7	766.6	43
896[a]	870[a]	848[a]	826[a]	805[a]	32

b. Cd|CdCl₂|Cl₂|C

600°	650°	700°	750°	Ref
1338	1310	1282	1255	40
1340	1311	1279	1246	45
1331[a]				32

c. Pb|PbCl₂|Cl₂|C

550°	600°	650°	700°	Ref
1247	1217	1187	1157	46
1234	1197	1161	1124	47
1248	1218	1195	1169	48
1244.8	1214.0	1182.4	1149.8	45
1248	1222	1195	1169	62
1242	1211	1180	1149	63
1242	1213	1183	1154	64
1243.6	1216.9	1190.2	1163.6	51
1243[a]	1215[a]	1187[a]	1159[a]	32
1246.5[a]	1218.2[a]	1190.6[a]	1163.4[a]	34

d. Zn|ZnCl₂|Cl₂|C

450°	500°	550°	600°	Ref
1627	1601	1574	1548	49
1593	1567	1536	1498	45
1607	1573	1540	1506	65
1607	1572	1538	1503	63
1599	1563	1529	1493	66
1598	1564	1530	1495	67
1629[a]	1603[a]	1577[a]	1552[a]	32

[a] Thermochemical data.

agreement between experimental and thermochemical $E°$ values. Significant departures are also observed between these two quantities, especially when the electrodes interact with the molten salt (see sections A and B).

TABLE II

$E°$ VALUES (mV) OF FORMATION CELLS WITH BROMIDES OR IODIDES AS LIQUID ELECTROLYTE AT VARIOUS TEMPERATURES (°C) AS CALCULATED FROM LITERATURE SOURCES BY MEANS OF A LINEAR AND A QUADRATIC LEAST-SQUARES ANALYSIS

a. Ag|AgBr|Br₂|C

450°	500°	550°	600°	Ref
798.8	784.4	769.9	755.5	70
800.7	786.4	772.0	757.6	72
795[a]	781[a]	767[a]	754[a]	32

b. Pb|PbBr₂|Br₂|C

400°	450°	500°	550°	600°	Ref
1133	1096	1045	979	899	71
1091	1063	1031	997	961	69
1092.5	1062.1	1031.8	1001.5	971.1	68
1094.4[a]	1061.8[a]	1031.2[a]	1002.7[a]	976.2[a]	32
1092.9[a]	1065.3[a]	1038.5[a]	1012.4[a]	987.1[a]	34

[a] Thermochemical data.

In cells where the anode and cathode are of different materials, a thermoelectric effect (thermocouple) should be anticipated as part of the measured emf. Various corrections for the thermoelectric effect have been applied, and these always introduce uncertainties in the determination of free energies from emf data. The influence of the thermoelectric effect on excess properties can be minimized by using the same experimental arrangement for the single salt and for the mixtures.

A. CELLS WITH THE CHLORINE|GRAPHITE ELECTRODE

The chlorine|graphite electrode consists of a graphite rod or a graphite tube suspended in the melt and over which or through which gaseous chlorine gas is passed. The proper operation of the electrode has been discussed by Senderoff and Mellors[35] and by Drossbach.[36] To attain a rapid equilibrium at the electrode both authors recommend short treatment by preelectrolysis. It was found by various investigators that pretreatment of the graphite electrode was necessary to assure equilibrium conditions. Senderoff and Mellors[35] pretreated the graphite rod by holding it in a chlorine atmosphere at 2300° for 2 hr. Panish, Blankenship, Grimes, and Newton[37] observed that unless the graphite electrode was first exposed to a chlorine atmosphere at 1000° for 10–20 hr, the emf's were erratic and required long equilibration periods. Leonardi and Brenet[38] exposed the graphite electrode in fuming hydrochloric acid, and Murgulescu and Sternberg[39] subjected the graphite rod to a 24-hr period of electrolysis in molten AgCl. Lantratov and Alabyshev[40] prepared the chlo-

(32) W. J. Hamer, M. S. Malmberg, and B. Rubin, *J. Electrochem. Soc.*, **103**, 8 (1965); 112, 750 (1965).

(33) W. J. Hamer, *J. Electroanal. Chem.*, **10**, 140 (1965).

(34) "JANAF Thermochemical Tables," Clearinghouse for Federal Scientific and Technical Information, The Dow Chemical Co., Midland, Mich. 48640.

(35) S. Senderoff and G. W. Mellors, *Rev. Sci. Instr.*, **29**, 151 (1958).

(36) P. Drossbach, *J. Electrochem. Soc.*, **103**, 700 (1956).

(37) M. B. Panish, F. F. Blankenship, W. R. Grimes, and R. F. Newton, *J. Phys. Chem.*, **62**, 1325 (1958).

(38) J. Leonardi and J. Brenet, *Compt. Rend.*, **261**, 116 (1965).

(39) I. G. Murgulescu and S. Sternberg, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **2**, 251 (1957).

(40) M. F. Lantratov and A. F. Alabyshev, *J. Appl. Chem. USSR*, **26**, 321 (1953).

rine electrode by heating it in a chlorine atmosphere at 750° for 3–4 hr and subsequently at 700° and at 400° for 20–24 hr alternately under vacuum and in chlorine, respectively.

The $Ag|AgCl|Cl_2|C$ cell consists of a silver wire and the chlorine|graphite electrode, both in contact with molten silver chloride. This cell has been used extensively, and various investigators have determined the excess properties of silver chloride containing melts by emf measurements. There are considerable differences between the reported data (Table I). Whereas good agreement between various authors is found in the temperature range from 500 to 600°, at higher temperatures the differences are more pronounced. While the reversibility of the silver electrode has been questioned,[41] the differences at higher temperatures are most likely due to improper pretreatment of the chlorine|graphite electrode.

Senderoff and Mellors[35] observed a linear temperature dependence of the free energy of formation of AgCl between 530 and 920° provided the chlorine|graphite electrode was pretreated as already mentioned. It was also recommended that a short period of electrolysis be used to attain equilibrium rapidly. In the experimental arrangement, the chlorine pressure was held at 1 atm, and the silver electrode was isolated from the chlorine by enclosing it in a quartz tube with a porous quartz disk at the bottom. The reported emf data were also corrected for the thermal emf of the $Ag|C$ couple for which literature values were chosen. By contrast, Leonardi and Brenet[38] and Panish, Blankenship, Grimes, and Newton[37] applied an experimentally determined correction for the thermal emf (1–9 mV), while Salstrom[42] used a thermal emf correction without giving the numerical values in the publication; no correction for this effect was reported by Stern.[43]

It is evident from this appraisal that, up to 600°, most of the reported data on AgCl correspond with equilibrium conditions. At higher temperatures some of the emf values are of questionable significance.

Liquid metals have been used as cation electrodes in emf cells, such as $Cd|CdCl_2|Cl_2|C$, $Pb|PbCl_2|Cl_2|C$, and $Zn|ZnCl_2|Cl_2|C$. Electrical contact with the molten metal is made by a higher melting metal that does not dissolve in the molten electrodes (W or Pt) or by a graphite rod. $CdCl_2$, $PbCl_2$, and $ZnCl_2$ are quite volatile and $ZnCl_2$ is also extremely hygroscopic. Special precautions are therefore important for the investigation of these cells. A further complication is the high solubility of cadmium and lead metals in the

molten halides of these metals. Recalculated experimental and thermochemical emf's for these cells are given in Tables Ib–d.

Lantratov and Alabyshev[40] recrystallized cadmium chloride from hydrochloric acid solutions and dried it in a stream of HCl. The cadmium metal was preheated by passing the molten metal through a narrow capillary under vacuum. Saturation of the chlorine electrode within 30–60 min was noted by these authors. It is known that some kinds of graphite and carbon react readily with $CdCl_2$ and Cl_2,[28,29,44] and, in this system, this may be a source of unstable and erratic potentials. The Lorenz and Velde[45] values for the cell, $Cd|CdCl_2|Cl_2|C$, are in good agreement with those of Lantratov and Alabyshev[40] (Table Ib). The corrections for the thermal emf of the $Cd|C$ couple are not given in the latter work[40] so that the magnitude of the correction cannot be assessed.

The most thorough investigation of the $Pb|PbCl_2|Cl_2|C$ cell appears to be that of Hagemark and Hengstenberg.[46] Thermal emf's were eliminated by making electrical contact with the molten lead using graphite. Inspection of Table Ic shows that most of the reported data are in reasonable agreement; the small differences are most possibly due to thermal emf's. The data reported by Hildebrand[47] are substantially lower, and this indicates that equilibrium conditions are not fulfilled when Cl_2 is generated at the electrode by simple electrolysis. On the other hand, it is remarkable that the data in which the polarization technique was used, e.g., Markov, Delimarskii, and Panchenko,[48] are in reasonable agreement with Hagemark and Hengstenberg.[46]

Inspection of the results in Table Id shows that the only emf study of the $Zn|ZnCl_2|Cl_2|C$ cell for which there is reasonable agreement with thermochemical data is that of Takahashi.[49] The $ZnCl_2$ was dried and pumped to remove oxides, and preelectrolyzed to remove traces of moisture. Takahashi also took due cognizance of the finite volatility of $ZnCl_2$ by correcting for its partial pressure with the assumption that $ZnCl_2$ and Cl_2 do not interact significantly in the vapor phase under the experimental conditions of this study.

The $Ce|CeCl_3|Cl_2|C$ and $Mg|MgCl_2|Cl_2|C$ cells can not be studied directly because of the high solubility of the metals in the single-salt melts and the further interactions of the dissolved metals with the molten halides. These systems have been studied indirectly

(41) T. Forland and C. G. M. Dijkhuis, Discussions Faraday Soc., 32, 161 (1961).

(42) E. J. Salstrom, J. Am. Chem. Soc., 56, 1272 (1934).

(43) K. Stern, J. Phys. Chem., 60, 679 (1956).

(44) W. Rudorff, Wien Chemiker-Ztg., 47, 1 (1944).

(45) R. Lorenz and H. Velde, Z. Anorg. Chem., 183, 81 (1929).

(46) H. Hagemark and D. Hengstenberg, J. Chem. Eng. Data, 11, 596 (1966).

(47) J. H. Hildebrand and G. C. Ruhle, J. Am. Chem. Soc., 49, 722 (1927).

(48) B. F. Markov, J. K. Delimarskii, and I. D. Panchenko, Zh. Fiz. Khim., 28, 1987 (1954).

(49) M. Takahashi, J. Electrochem. Soc. Japan, 28, E117 (1960).

using alloys as cation electrodes. Senderoff, Mellors, and Bretz[50] observed a stable emf for the cell, Ce–Sn|Ce-Cl₃, dilute in KCl|Cl₂|C, but for the corresponding system with pure Ce as the electrode, i.e., Ce|CeCl₃ dilute in KCl|Cl₂|C, a continuous drift was noted. Salient requirements for suitable alloy electrodes were specified as follows: the diluent metal in the alloy should be quite noble compared to cerium; the alloy should consist of two phases over a considerable range of composition (for constant activity of Ce); the activity of cerium in the alloy should be low; the alloy must behave reversibly as a $Ce^{3+}|Ce^0$ electrode. Senderoff, Mellors, and Bretz[50] found that these requirements were met in the Ce–Sn|CeCl₃|Cl₂|C cell. The system Ce–Bi|CeCl₃|Cl₂|C was investigated by Neil[51] and Neil, Clark, and Wiswall;[52] various compositions of the alloy were used and the activity of Ce in the Ce–Bi alloy was calculated from the alloy composition and published data for alloy activities. Some uncertainties are inevitably introduced in such calculations.

The Mg|MgCl₂|Cl₂|C cell has been studied by the decomposition potential technique.[45,53] A comparison between the "decomposition potential $E°$" and thermochemical $E°$ shows appreciable differences between these two sets of values. The cause for this discrepancy may be, in part, due to the solubility of Mg in molten MgCl₂ but, more likely, is due to the fact that the decomposition potential technique is not an equilibrium method. Neil, Clark, and Wiswall[52] used a magnesium alloy electrode in the Mg–Bi|MgCl₂|Cl₂|C cell in order to bypass the problems arising from the solubility of the metal in its molten chloride.

While cells such as Be|BeCl₂,NaCl|Cl₂|C,[54–58] Mn|MnCl₂,NaCl or KCl|Cl₂|C,[59] and Pu|PuCl₃,NaCl or KCl|Cl₂|C[60,61] have been studied, the experimental $E°$ cannot be obtained because these metals react with the single salts in the molten state. Reliable and tested thermochemical data for such systems having the single salts as liquid electrolytes are not known.

Some other investigations in which the Cl₂|C electrode was used[62–67] will be discussed in section IV.

B. CELLS WITH Br₂|C,I₂|C AND NO₂–O₂|Pt AS ANION ELECTRODES

Salstrom and Hildebrand[68] and Salstrom[69] noted that equilibrium at the Br₂|C electrode could be attained in 1–2 hr if the C rod was first heated in Br₂ (at several atmospheres pressure) and then in an oxygen flame. Without this pretreatment, 18–20 hr was required before a stable emf was obtained. Murgulescu and Marchidan[70] pretreated the graphite electrode in a Br₂ atmosphere and subsequently by electrolysis in molten AgBr to saturate the electrode. Lantratov and Shevlyakova[71] used a thin-walled graphite tube as a Br₂ electrode. The tube was saturated with Br₂ and then heated for 1.5 hr in the temperature range of 700–750°. $E°$ values of cells with a single molten bromide as electrolyte and the graphite|bromine electrode are compared in Table II.

Inspection of Table IIa shows, for the Ag|AgBr|Br₂|C cell, that there is good agreement between thermochemical data and experimental $E°$ values of Salstrom and Hildebrand[72] and Murgulescu and Marchidan.[70] The differences are most likely due to different corrections for thermoelectric effects.

The $E°$ for the Pb|PbBr₂|Br₂|C cell reported by Salstrom and Hildebrand[68] and Salstrom[69] are in reasonable agreement with thermochemical data, whereas the values as reported by Lantratov and Shevlyakova[71] differ significantly. These results are given in Table IIb.

The Cd|CdBr₂|Br₂|C cell was investigated by Lantratov and Shevlyakova.[73] The $E°$ values are found to differ significantly from thermochemical data (e.g., a difference of 41 mV at 600°).

The only investigations in which the iodine|graphite electrode has been used are those of Sternberg, Adorian,

(50) S. Senderoff, G. W. Mellors, and R. I. Bretz, Ann. N. Y. Acad Sci., 79, 878 (1960).

(51) D. E. Neil, "Thermodynamic Properties of Molten Chloride Solutions," Ph.D. Thesis, Rensselaer Polytechnic Institute, 1959; Dissertation Abstr., 20, 2591 (1960).

(52) D. E. Neil, H. M. Clark, and R. H. Wiswall, Jr., J. Chem. Eng. Data, 10, 21 (1965).

(53) B. F. Markov, J. K. Delimarskii, and I. D. Panchenko, Zh. Fiz. Khim., 29, 51 (1955).

(54) R. S. Sethi and H. L. Jindal, Current Sci., 34, 284 (1965).

(55) T. Kuroda and D. Matsumato, J. Electrochem. Soc., Japan, 33, 29 (1965).

(56) J. K. Delimarskii and E. M. Skobets, Zh. Fiz. Khim., 20, 1005 (1946).

(57) I. N. Sjejko and J. K. Delimarskii, Ukr. Khim. Zh., 25, 295 (1959).

(58) B. F. Markov and J. K. Delimarskii, Zh. Fiz. Khim., 31, 2589 (1957).

(59) M. Bruneaux, S. Ziolkiewicz, and G. Morand, Compt. Rend., 257, 3591 (1963); J. Chim. Phys., 61, 1215 (1964).

(60) R. Renz, J. Phys. Chem., 65, 1056 (1961).

(61) R. Benz and J. A. Leary, ibid., 65, 1056 (1961).

(62) M. F. Lantratov and A. F. Alabyshev, Zh. Prikl. Khim., 26, 263 (1953); J. Appl. Chem. USSR, 26, 235 (1953).

(63) A. Wachter and J. H. Hildebrand, J. Am. Chem. Soc., 52, 4655 (1930).

(64) Y. Nakamura and J. Brenet, Compt. Rend., 262C, 673 (1966).

(65) D. B. Marsland, "A Reference Electrode for Fused-Salt Studies," Ph.D. Thesis, Cornell University, 1958; Dissertation Abstr., 19, 1222 (1958).

(66) B. F. Markov and S. V. Volkov, Ukr. Khim. Zh., 30, 341 (1964).

(67) M. F. Lantratov and A. F. Alabyshev, Zh. Prikl. Khim., 27, 722 (1954); J. Appl. Chem. USSR, 27, 685 (1954).

(68) E. J. Salstrom and J. H. Hildebrand, J. Am. Chem. Soc., 52, 4641 (1930).

(69) E. J. Salstrom, ibid., 55, 1029 (1933).

(70) I. G. Murgulescu and D. I. Marchidan, Rev. Chim. Acad. Rep. Populaire Roumaine, 3, 47 (1958).

(71) M. F. Lantratov and T. N. Shevlyakova, Russ. J. Inorg. Chem., 4, 523 (1959).

(72) E. J. Salstrom and J. H. Hildebrand, J. Am. Chem. Soc., 52, 4650 (1930).

(73) M. F. Lantratov and T. N. Shevlyakova, Zh. Prikl. Khim., 4, 1065 (1961).

and Galasiu.[74-76] The difficult goal of constructing a reversible iodine electrode was achieved by maintaining the iodine in the gaseous state from the moment of generation to its removal from the cell. It was noted that the graphite electrode had to be in contact with iodine for 20 hr before stable potentials were attained. If a preelectrolysis was used the potentials stabilized in 5–6 hr. The agreement between experimental emf's and thermochemical values for the Ag|AgI|I₂|C cell is reasonable.

A reversible nitrate electrode has been devised by Ketelaar and Dammers-de Klerk.[77] It was found that a three-phase contact between the NO₂-O₂ mixture, the molten nitrate, and platinum was essential for a reproducible and stable electrode system. The excellent agreement between the experimental $E°$ for the Ag|AgNO₃|O₂-NO₂|Pt cell and thermochemical data confirm the reversible behavior of this nitrate electrode.

C. CELLS IN WHICH GLASS FUNCTIONS AS A CATION INDICATOR ELECTRODE

Glass has been used extensively as an electrically conducting membrane for the separation of two molten salt phases.[78-83] However, the use of glass as an indicator electrode, without liquid junction, is a more recent innovation.[25-31,84] The applicability of alkali glasses for indicator electrodes has been investigated by Forland and Ostvold[26] and Ostvold.[25,27,84] It was found from transport measurements that the electrical contact through glass in cells such as C|Cl₂|NaCl|alkali glass|NaCl,MgCl₂|Cl₂|C was by sodium ions only. The same was true for cells containing NaCl,CaCl₂, NaCl,SrCl₂, and NaCl,BaCl₂ mixtures. The emf of the above cells corresponded with the difference in the chemical potential of NaCl in the mixture and the chemical potential of NaCl as a single molten salt.

Dijkhuis and Ketelaar[28,29] investigated the W|Cd| CdCl₂,NaCl|Pyrex glass|CdCl₂(x = 0.6),NaCl(x = 0.4)|Cd|W cells. From the stability of the emf and from the concentration dependence of emf's in dilute solutions, it was confirmed that the transport number of sodium was unity in these cells. Starting with the total cell reaction a relation was derived[28,29] between emf and excess properties of mixtures.

Sternberg and Herdlicka[31] have investigated cells such as C|Br₂|NaBr|glass|NaBr,NaCl|Br₂|C. In these cells only one kind of cation is on both sides of the glass. Since the ionic mobility of cations is greater than the ionic mobility of anions in glass, the glass functions as a cation electrode. In silver halide, sodium halide mixtures (dilute in Na⁺) and using silica for the separation of the melts, Stern and Meador[79] found the transport number for the sodium ion to be 1.0.

From various recent investigations it is apparent that knowledge of the free energy of formation of "undercooled" molten alkali halides is helpful for the interpretation of emf data of equilibrium cells in which glass functions as a cation selective membrane. Such free energies of formation cannot be determined by the emf method because alkali metals cannot be used as electrodes. The thermochemical data for the free energy of formation of alkali halides are known;[32-34] these are summarized, in millivolts, in Table III.

TABLE III

$E°$ (mV) = $a + bT + cT^2$ FOR SOME CELLS, ALKALI METAL|ALKALI HALIDE|HALIDE|C[a,b]

	a	$b \times 10^3$	$c \times 10^6$	Temp range, °C
Li|LiF|F₂|C	5890.1	−830.4	64.0	926–1226
Li|LiCl|Cl₂|C	3830.9	−573.3	0.0	626–926
Li|LiBr|Br₂|C	3469.0	−668.8	91.1	626–926
Li|LiI|I₂|C	2829.0	−626.2	88.5	526–826
Na|NaF|F₂|C	6206.5	−1809.2	113.8	1026–1326
Na|NaCl|Cl₂|C	2830.4	1746.1	−1536.2	826–1126
Na|NaBr|Br₂|C	2497.6	1803.8	−1559.7	826–1126
Na|NaI|I₂|C	1553.3	2725.8	−2061.8	726–1026
K|KF|F₂|C	6015.5	−1707.9	106.0	926–1226
K|KCl|Cl₂|C	4708.6	−1680.8	141.6	826–1126
K|KBr|Br₂|C	5085.7	−3106.5	922.4	826–1126
K|KI|I₂|C	3188.6	68.6	−744.0	726–1026

[a] T in °C.   [b] The parameters a, b, and c have been generated from thermochemical literature values[34] by a linear and a quadratic least-squares analysis.

III. THEORETICAL PRINCIPLES AND METHOD OF CALCULATION

To gain meaningful comparisons between the free-energy values from the various investigations, and in order to be able to compare excess free energies with heats of mixing data, recalculation in a systematic manner appeared essential, starting with results of the original emf data of each contribution. The following are the basic principles and concepts used for this purpose.[85] The excess molar Gibbs free energy of mixing (G^E) of a molten binary mixture AX(1 − x),

(74) S. Sternberg, I. Adorian, and I. Galasiu, *J. Chim. Phys.*, **63**, 62 (1965).

(75) S. Sternberg, I. Adorian, and I. Galasiu, *Electrochim. Acta*, **11**, 385 (1966).

(76) S. Sternberg, I. Adorian, and I. Galasiu, *Rev. Roumaine Chim.*, **11**, 581 (1966).

(77) J. A. A. Ketelaar and A. Dammers-de Klerk, *Rec. Trav. Chim.*, **83**, 322 (1964).

(78) K. H. Stern, *Chem. Rev.*, **66**, 355 (1966).

(79) K. H. Stern and S. E. Meador, *J. Res. Natl. Bur. Std.*, **A69**, 553 (1965).

(80) J. O. M. Bockris, G. J. Hills, D. Inman, and L. Young, *J. Sci. Instr.*, **33**, 438 (1956).

(81) R. J. Labrie and V. Lamb, *J. Electrochem. Soc.*, **106**, 895 (1959).

(82) R. Littlewood, *Electrochim. Acta*, **3**, 270 (1961).

(83) G. J. Janz and A Conte, *ibid.*, **9**, 1269 (1964).

(84) T. Ostvold, *Acta Chem. Scand.*, **20**, 2320 (1966).

(85) C. G. M. Dijkhuis and G. J. Janz, Rensselaer Polytechnic Institute, unpublished work, 1967.

BX(x) may be expressed at a certain temperature by the equation

$$G^E = x(1 - x)(a + bx + cx^2) \quad (1)$$

The expressions for the excess chemical potentials of the components AX and BX (μ^E_{AX} and μ^E_{BX}) follow readily from eq 1 and the Gibbs–Duhem relation, *i.e.*

$$\mu^E_{AX} = [a - b + 2(b - c)x + 3cx^2]x^2 \quad (2a)$$

and

$$\mu^E_{BX} = (a + 2bx + 3cx^2)(1 - x)^2 \quad (2b)$$

The values of the constants a, b, and c may be obtained from a graphical analysis of μ^E_A/xx^2 or $\mu^E_{BX}/(1 - x)^2$ as a function of the mole fractions, *i.e.*

$$\mu^E_{AX}/x^2 = a - b + 2(b - c)x + 3cx^2 \quad (3a)$$

and

$$\mu^E_{BX}/(1 - x)^2 = a + 2bx + 3cx^2 \quad (3b)$$

By expressing the excess entropy (S^E) according to the equation

$$S^E = x(1 - x)(a' + b'x + c'x^2) \quad (4)$$

it follows similarly that

$$s^E_{AX}/x^2 = a' - b' + 2(b' - c')x + 3c'x^2 \quad (5a)$$

and

$$s^E_{BX}/(1 - x)^2 = a' + 2b'x + 3c'x^2 \quad (5b)$$

The parameters a', b', and c' in eq 5 may be determined from an analysis of s^E_{AX}/x^2 or $s^E_{BX}/(1 - x)^2$ as a function of x.

The excess chemical potentials (eq 3a and 3b) and the excess entropies (eq 5a and 5b) can be determined from experimental emf data. Consider the cell

$$Pb | PbCl_2(1 - x),NaCl(x) | Cl_2 | C$$

A

The cell reaction is

$$Pb + Cl_2 \rightarrow PbCl_2 \text{ (two-electron transfer)} \quad (6)$$
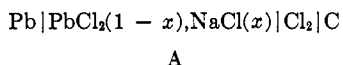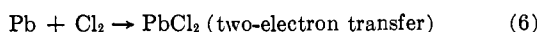
from which it follows that

$$-2EF = \mu_{PbCl_2} - \mu_{Pb} - \mu_{Cl_2} \quad (7)$$

If one now defines ideal solution behavior by means of the Temkin relation[86]

$$\mu_{PbCl_2} = \mu^\circ_{PbCl_2} + RT \ln (1 - x) + \mu^E_{PbCl_2} \quad (8)$$

it can be shown from eq 7 and 8 that

$$-2EF = \mu^\circ_{PbCl_2} + RT \ln (1 - x) +$$
$$\mu^E_{PbCl_2} - \mu_{Pb} - \mu_{Cl_2} \quad (9)$$

For the case where the electrolyte is pure $PbCl_2$ (*i.e.*, $x = 0$, the emf of this cell is given by

$$-2E^\circ F = \mu^\circ_{PbCl_2} - \mu_{Pb} - \mu_{Cl_2} \quad (10)$$

Combining eq 9 and 10 gives

$$-2(E - E^\circ)F = RT \ln (1 - x) + \mu^E_{PbCl_2} \quad (11)$$

When E and μ are expressed in millivolts, the result is

$$\mu^E_{PbCl_2} = 2(E - E^\circ)F + 0.19845T \log (1 - x) \quad (12)$$

Thus if follows that, from a knowledge of E, E°, and x, a measure of the excess free energies can be gained by this method.

The partial excess entropy can be gained from the temperature dependence of the E values, *i.e.*

$$s^E_{PbCl_2} = -(\mu^E_{PbCl_2}/T)_x = 2(E^\circ/T)_x - 2(E/T)_x - 0.19845 \log (1 - x) \quad (13)$$

Thus $s^E_{PbCl_2}$ may be gained from the temperature dependence of $\mu^E_{PbCl_2}$ (eq 12), whereas the parameters a', b', and c' in eq 4 may be obtained from an analysis of $s^E_{PbCl_2}/x^2$ as a function of x (eq 5).

Thermodynamic properties of molten salts have also been determined from cells in which glass functions as a cation selective membrane. Consider the cell

$$\underbrace{C | Cl_2 | NaCl | glass}_{I} | \underbrace{NaCl(1 - x),MgCl_2(x) | Cl_2 | C}_{II}{}^{25}$$

B
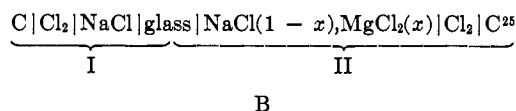
The cell reaction was found to be [25,27]

$$(NaCl)_I \rightarrow (NaCl)_{II} \quad (14)$$

from which it follows that

$$-EF = (\mu_{NaCl})_{II} - (\mu_{NaCl})_I \quad (15)$$

Again defining ideal mixing behavior by means of the Temkin relation[86] and expressing E and μ in millivolts

$$\mu^E_{NaCl} = E + 0.19845T \log (1 - x) \quad (16)$$

Excess free energies and excess entropies can now be calculated from the experimental emf's of cell B analogous to the procedure for cell A.

IV. EXCESS FREE ENERGIES OF BINARY MIXTURES WITH A COMMON ION

A. MIXTURES WITH A COMMON ANION

1. Mixtures $AgCl,MCl_n$ ($M = Li$, Na, K, Pb); $AgBr,MBr_n$ ($M = Li, Na, K, Rb, Pb$); and AgI,KI

Free energies of mixing of the systems $AgCl,MCl_n$ ($M = Li$, Na, K, Pb) have been determined by means of emf measurements on cells, such as $Ag | AgCl$, $MCl_n | Cl_2 | C$. It was pointed out in section II.A that special pretreatment of the chlorine|graphite electrode is necessary in order to attain equilibrium potentials at higher temperatures. The excess properties, shown in Figure 1, were calculated as outlined in the preceding section; the temperature selected is one that ensures

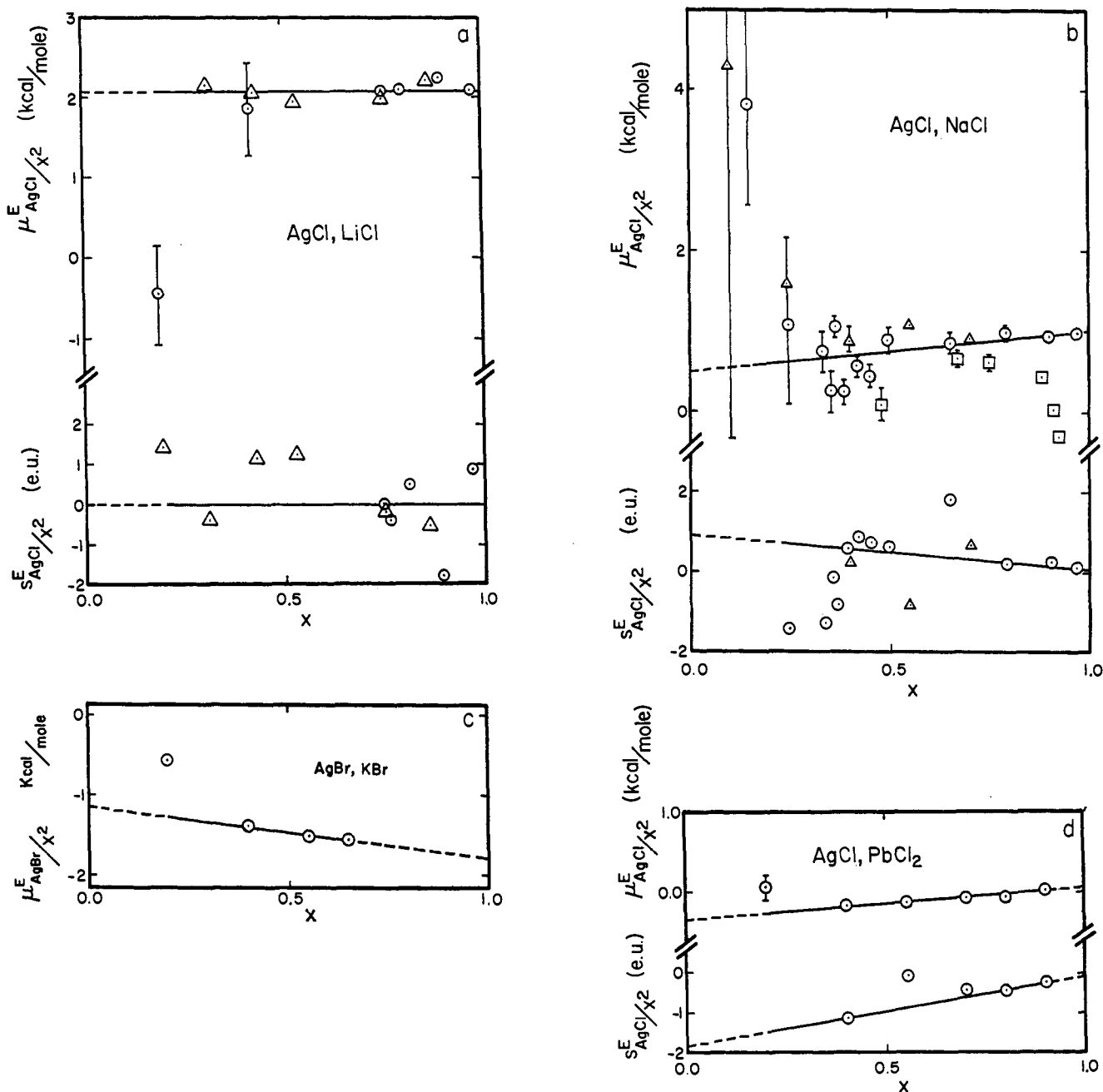(86) M. Temkin, *Acta Physicochim. USSR*, **20**, 411 (1945).

Figure 1.—Experimental values of $\mu^E{}_{AgCl}/x^2$ and $s^E{}_{AgCl}/x^2$ in molten binary chloride mixtures. The limits of uncertainty and the solid lines are the results of the present analysis. (a) $AgCl(1 - x),LiCl(x)$: o, Panish, Newton, Grimes, and Blankenship,[88] 800°; △, Salstrom, Kew, and Powell,[87] 600°. (b) $AgCl(1 - x),NaCl(x)$: o, Panish, Blankenship, Grimes, and Newton,[37] 800°; ⊡, Stern,[90] 800°; △, Sternberg and Gheorghiu,[89] 800°. (c) $AgCl(1 - x),KCl(x)$: △, Murgulescu and Sternberg,[39] 650°; o, Stern,[43] 700°. (d) $AgCl(1 - x),PbCl_2(x)$: o, Salstrom,[42] 550°.

reversible behavior for the chlorine|graphite electrode and the broadest possible concentration range. The recalculated excess properties are presented in Figure 1. The Ag|AgCl,LiCl|Cl₂|C cells were studied by Salstrom, Kew, and Powell[87] and by Panish, Newton, Grimes, and Blankenship.[88] In both investigations, precautions

were taken to exclude contaminants from the molten salts. The two sets of data were combined to generate the excess free energy for the mixture AgCl,LiCl. The results are illustrated in Figure 1a. The excess entropy values are too scattered for an accurate determination of the parameters in eq 4. Inspection of Figure 1a shows that the excess entropy is certainly small and has a tendency to be slightly positive.

The AgCl,NaCl mixtures have been studied by Panish, Blankenship, Grimes, and Newton,[37] by

(87) E. J. Salstrom, T. J. Kew, and T. M. Powell, *J. Am. Chem. Soc.*, **58**, 1848 (1936).

(88) M. B. Panish, R. F. Newton, W. R. Grimes, and F. F. Blankenship, *J. Phys. Chem.*, **63**, 668 (1959).

Sternberg and Gheorghiu,[89] and by Stern.[90] The $E°$ values of these authors have been discussed in section II.A, and it was pointed out there that the emf values of two of these studies[37,89] correspond with equilibrium conditions; the excess free energies were therefore determined by combining the data of these two studies; the excess entropies (Figure 1b) were gained from the temperature dependence of the emf's of Panish, Blankenship, Grimes, and Newton.[37]

The $Ag|AgCl,KCl|Cl_2|C$ systems were investigated by Murgulescu and Sternberg[39] and by Stern.[43] In Table I it is seen that the Murgulescu and Sternberg values[39] give best agreement with equilibrium $E°$ values, and these data were used to calculate the excess free energy accordingly (Figure 1c). The $s^E{}_{AgCl}/x^2$ values are too scattered for even an estimate of S^E.

The low-melting mixture $AgCl,PbCl_2$ was studied by Salstrom.[42] Inspection of Table I shows that the $E°$ values of Salstrom correspond with equilibrium conditions. In this work dry hydrogen chloride was bubbled through the melt to attain high purity. The emf studies also spanned a broad concentration range; there is little doubt that the results are of a high quality. As shown in Figure 1d, this mixture has a nearly ideal free energy of mixing, but it is certainly not a regular solution, and the excess entropy of mixing is significant.

The systems $AgBr,MBr_n$ (M = Li, Na, K, Rb, Pb) have been investigated by emf measurements on cells in which a silver wire functions as silver electrode and a bromine|graphite electrode as bromine|bromine electrode. The excess free energy of the mixture $AgBr,LiBr$ was determined by Salstrom and Hildebrand[72] from the cells $Ag|AgBr,LiBr|Br_2|C$. The $E°$ values indicate reversibility of the electrodes (section II.B). Furthermore, air was excluded and hydrolysis products from the melt were removed using a stream of dry hydrogen bromide. These factors support the view that the excess free energy and the excess entropy, determined from Figure 2a, are of high accuracy.

The mixtures $AgBr,NaBr$, $AgBr,KBr$, and $AgBr,Rb-Br$ were investigated by Salstrom[91–93] using the same technique as for mixtures $AgBr,LiBr$. The excess properties of these silver bromide–alkali bromide mixtures are illustrated in Figure 2. It is seen that the random error is appreciable, possibly because only a limited concentration range was investigated.

The studies of the low-melting mixture, $AgBr,PbBr_2$, extended over nearly the whole concentration range.[94] As shown in Figure 2e, it is found that the excess free

energy of this mixture is very nearly zero. The mixture, however, is certainly not a regular solution. A graph of $s^E{}_{AgBr}/x^2$ for this mixture, as shown in Figure 2e, indicates that the excess entropy of mixing is also very nearly zero.

Excess properties of the mixture AgI,KI have been determined by Sternberg, Adorian, and Galasiu[75] from cells of the type $Ag|AgI,KI|I_2|C$, using a reversible $I_2|C$ electrode assembly. The agreement between the experimental $E°$ and the thermochemical value for the free energy of formation (section II.B) is reasonable so that excess properties of relatively high accuracy may be derived from these data. The recalculated excess properties for this mixture are illustrated in Figure 3; inspection shows that the excess entropy is exceptionally asymmetrical.

2. Mixtures $CdCl_2,MCl_n$ (M = Na, K, Ba); $CdBr_2,KBr$; and CdI_2,NaI

Lantratov and Alabyshev[40] determined free energies of mixing of the system $CdCl_2,NaCl$ by emf studies of $Cd|CdCl_2,NaCl|Cl_2|C$ cells. Dijkhuis and Ketelaar[28,29] overcame difficulties resulting from the high solubility of Cd metal in the single molten salt $CdCl_2$ by selecting cells of the type $W|Cd|CdCl_2,NaCl|glass|$ $CdCl_2(x = 0.6)$, $NaCl(x = 0.4)|Cd|W$, in which glass functions as a sodium ion indicator electrode. The two sets of data are compared in Figure 4a. Although the values deviated from each other, the agreement is all that could be expected when it is realized that the Lantratov and Alabyshev[40] data were gained by subtracting the emf's of cells with mixtures from the $E°$ of cells for which there is a relatively high solubility of the metal in the single-salt melt.

The excess free energies of systems $CdCl_2,KCl$ and $CdCl_2,BaCl_2$ were investigated by Lantratov and Alabyshev,[40] using formation cells having Cd metal and chlorine|graphite electrodes. As already noted, an uncertainty is involved due to the high solubility of Cd metal in the single molten salt, $CdCl_2$. Nevertheless the $\mu^E{}_{CdCl_2}/x^2$ vs. x graphs for the $CdCl_2,KCl$ and $CdCl_2,BaCl_2$ mixtures are much more reasonable than for the $CdCl_2,NaCl$ mixture (e.g., Figures 4b and 4c). This could be understood if the absolute value of the excess free energy for the system $CdCl_2,NaCl$ is small compared to the excess free energy for the other two mixtures; the relative influence of the Cd solubility on the excess free energy would thus be smaller.

The excess entropy data of the $CdCl_2$ mixtures are too scattered for an accurate evaluation, but an insight as to the trend can be gained from an analysis of the temperature dependence of the emf data of Lantratov and Alabyshev[40] (e.g., Figure 4).

The systems $Cd|CdBr_2,KBr|Br_2|C$ were investigated by Lantratov and Shevlyakova.[73] In section II.B

(89) S. Sternberg and S. Gheorghiu, *Studii Cercet. Chim. Acad. Rep. Populaire Roumaine,* **7**, 107 (1959).
(90) K. H. Stern, *J. Phys. Chem.,* **62**, 385 (1958).
(91) E. J. Salstrom, *J. Am. Chem. Soc.,* **53**, 1794 (1931).
(92) E. J. Salstrom, *ibid.,* **53**, 3385 (1931).
(93) E. J. Salstrom, *ibid.,* **54**, 4252 (1932).
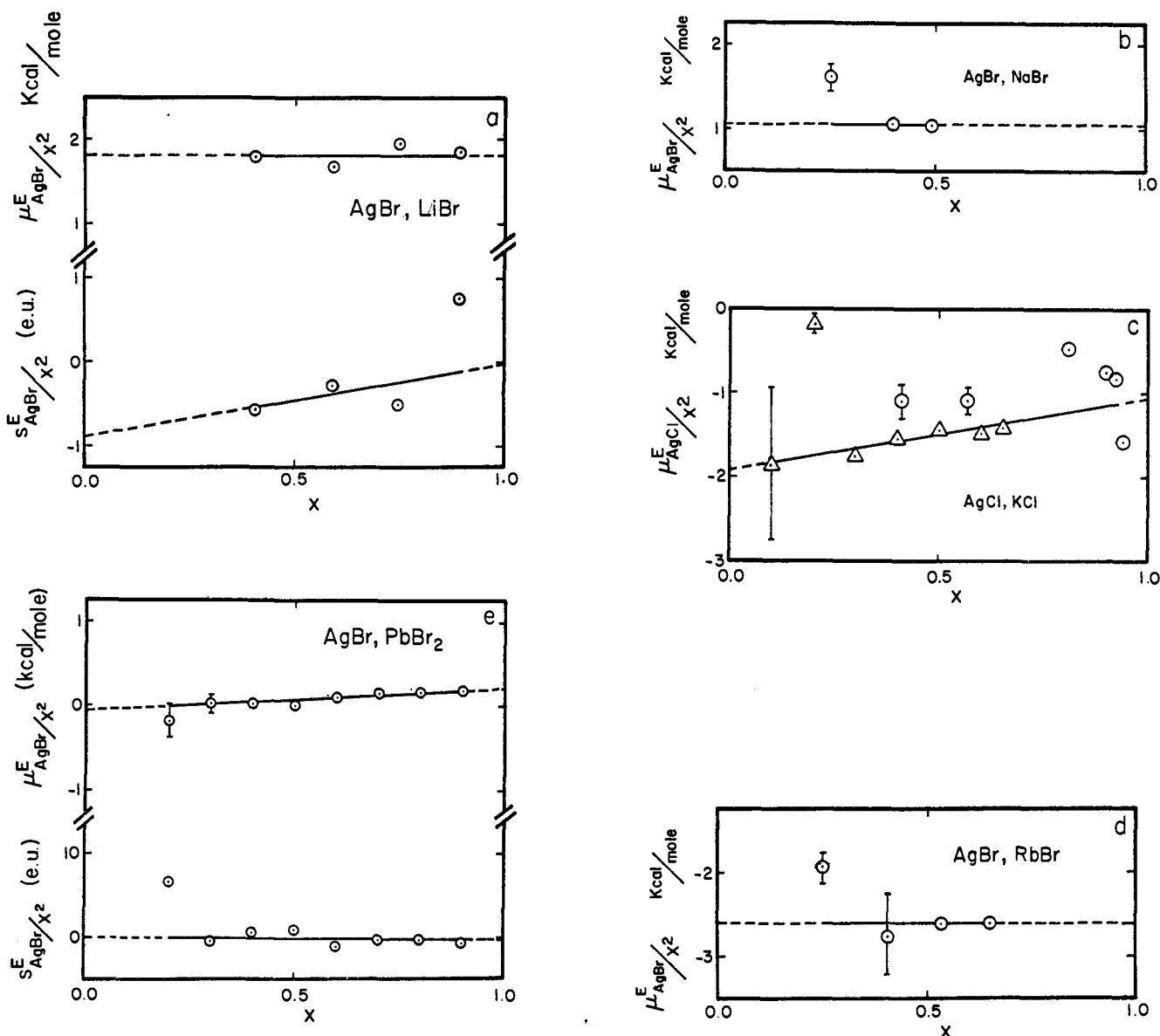(94) E. J. Salstrom, *ibid.,* **54**, 2653 (1932).

Figure 2.—Experimental values of μ^E_{AgBr}/x^2 and s^E_{AgBr}/x^2 in molten binary bromide mixtures. The limits of uncertainty and the solid lines are the result of the present analysis. (a) AgBr(1 − x),LiBr(x), Salstrom and Hildebrand,[72] 550°; (b) AgBr(1 − x),NaBr(x), Salstrom,[91] 600°; (c) AgBr(1 − x),KBr(x), Salstrom,[92] 600°; (d) AgBr(1 − x),RbBr(x), Salstrom,[93] 550°; (e) AgBr(1 − x),PbBr$_2$(x), Salstrom,[94] 550°.

it was noted that the $E°$ thus determined differs from the thermochemically based values. Nevertheless the $\mu^E_{CdBr_2}/x^2$ graphical analysis is reasonably linear so that the excess thermodynamic properties were calculated from these emf data. The results are illustrated in Figure 4d.

The CdI$_2$,NaI mixture was investigated by Dijkhuis and Ketelaar[28,29] by emf studies using cells such as W|Cd|CdI$_2$,NaI|glass|CdI$_2$(x = 0.6),NaI(x = 0.4)| Cd|W; as previously noted the glass is a sodium indicator electrode. If concentrated CdI$_2$ mixtures are avoided, the solubility of Cd in the molten CdI$_2$ does not influence the excess properties derived from these data.

3. Mixtures $CeCl_3,MCl_n$ ($M = Na, K, Ca$)

Because of the high solubility of Ce in the molten CeCl$_3$, the free-energy values for melts containing CeCl$_3$ cannot be determined from emf studies of systems in which cerium metal is used as an electrode material. Senderoff, Mellors, and Bretz[50,95] and Neil[51] thus utilized cerium alloys as indicator electrodes (section II.A). The $\mu^E_{CeCl_3}/x^2$ vs. x relationships for CeCl$_3$,NaCl, CeCl$_3$,KCl, and CeCl$_3$,CaCl$_2$ are shown in Figure 5. Senderoff, Mellors, and Bretz[50,95] used a Ce–Sn alloy, whereas Neil[51] used a Ce–Bi alloy as the Ce^{3+} electrodes.

(95) S. Senderoff, G. W. Mellors, and R. I. Bretz, J. Electrochem. Soc., 108, 93 (1961).

For $CeCl_3$,KCl there is an appreciable deviation between the values derived from these two studies. Neil[51] worked with alloys of various compositions and calculated the activity of Ce in each alloy, whereas Senderoff, Mellors, and Bretz[50,95] fixed the alloy composition as a constant. The results from the latter study are possibly more accurate although the two techniques should give equivalent results if the Ce activity in the various alloys is known exactly.

4. Mixtures $MgCl_2,MCl_n$ ($M = Li, Na, K, Rb$)

Binary magnesium chloride–alkali chloride mixtures have been investigated with three different types of electrochemical cells. Markov, Delimarskii, and Panchenko[53] used a nonequilibrium method (current–voltage measurements and extrapolation to zero current) to determine the cell emf. Systematic errors are involved in excess free energies derived from this kind of cell, and the data are, at best, only sufficient for an estimate of the order of magnitude of the excess free energy. A Mg–Bi alloy and a chlorine|graphite electrode under equilibrium conditions were used by Neil, Clark, and Wiswall[52] (section II.A).

Ostvold[25] used emf cells with a sodium-specific glass as the sodium indicator electrode for studies of $MgCl_2$,NaCl mixtures (section II.C).

The $MgCl_2$,LiCl mixture has been studied by Markov, Delimarskii, and Panchenko[53] using the nonequilibrium current–voltage technique. A straight-line relationship for $\mu^E_{MgCl_2}/x^2$ vs. x, as seen in Figure 6a, is observed. It is also found from the comparison of these data with equilibrium data for the mixtures $MgCl_2$,NaCl and $MgCl_2$,KCl that the excess properties are of the correct order of magnitude.

For the system $MgCl_2$,NaCl, investigated by the three above-mentioned techniques, it should be noted that the chemical potential of $MgCl_2$ in the mixture was measured by Markov, Delimarskii, and Panchenko[53] and Neil, Clark, and Wiswall,[52] whereas the chemical potential of NaCl was studied by Ostvold.[25] It follows that the equilibrium values of Neil, Clark, and Wiswall[52] are the most accurate for $MgCl_2$-rich binary mixtures, and the Ostvold values[25] are the most accurate for NaCl-rich binary mixtures. The excess free energies were calculated by weighting the two sets of data accordingly; the results are compared in Figures 6b and 6c with the values from the individual investigations. From the temperature dependence of the emf data,[25,53] an insight on the excess entropy can be gained. Whereas the results from the nonequilibrium method[53] indicate an extremely high positive excess entropy, a slightly negative excess entropy is predicted from the equilibrium data of Ostvold;[25] this is illustrated in Figure 6c.

The $MgCl_2$,KCl mixture was similarly studied by Neil, Clark, and Wiswall[52] and Markov, Delimarskii,

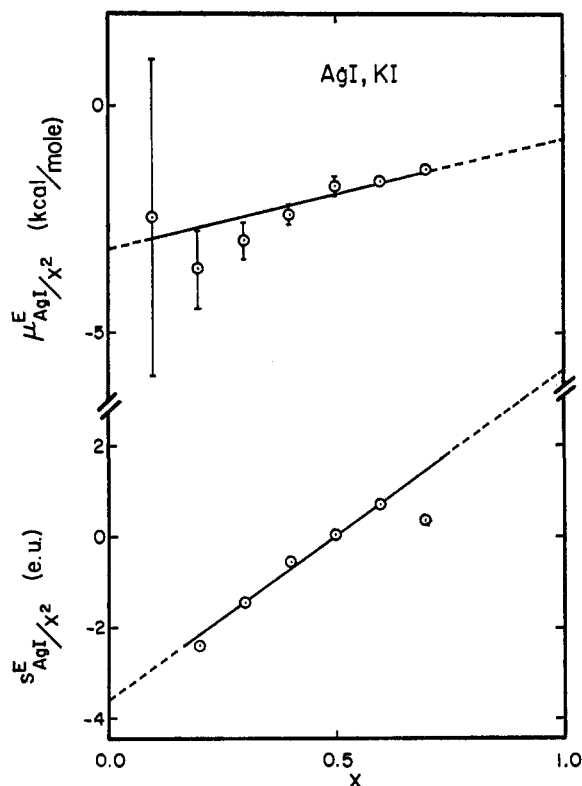Figure 3.—Experimental values of μ^E_{AgI}/x^2 in the molten binary mixture AgI,KI(x). The solid line and the limits of uncertainty are the result of the present analysis: ⊙, Sternberg, Adorian, and Galasiu,[75] 600°.

and Panchenko.[53] As already noted, the results from the equilibrium technique[52] are the more accurate and were used to derive the excess free energies; these are shown in Figure 6d. The $MgCl_2$,RbCl system has been studied by Markov, Delimarskii, and Panchenko[53] using the nonequilibrium technique; the excess free energy from these data (Figure 6c) are to be taken as an order of magnitude only.

5. Mixtures $NaCl,MCl_n$ ($M = Ca, Ba, Sr$)

Cells, such as $C|Cl_2|NaCl|glass|CaCl_2(1 - x)$,NaCl($x$)$|Cl_2|C$ and the corresponding arrangement with $SrCl_2$ and $BaCl_2$ in place of $CaCl_2$ were investigated by Ostvold.[25,27] As noted elsewhere (section II.C), it was establsished that the specially prepared glasses function as sodium indicator electrodes. The results from these studies were used to generate the excess free energy and the excess entropy, as illustrated in Figure 7.

6. Mixtures $PbCl_2,MCl_n$ ($M = Li, Na, K, Rb, Cs, Ca,$ Sr, Ba, Zn); $PbBr_2,MBr_n$ ($M = Na, Zn$); and PbI_2,NaI

The excess free energies for the $PbCl_2$,NaCl system have been determined from studies of the Pb|PbCl_2,Na-
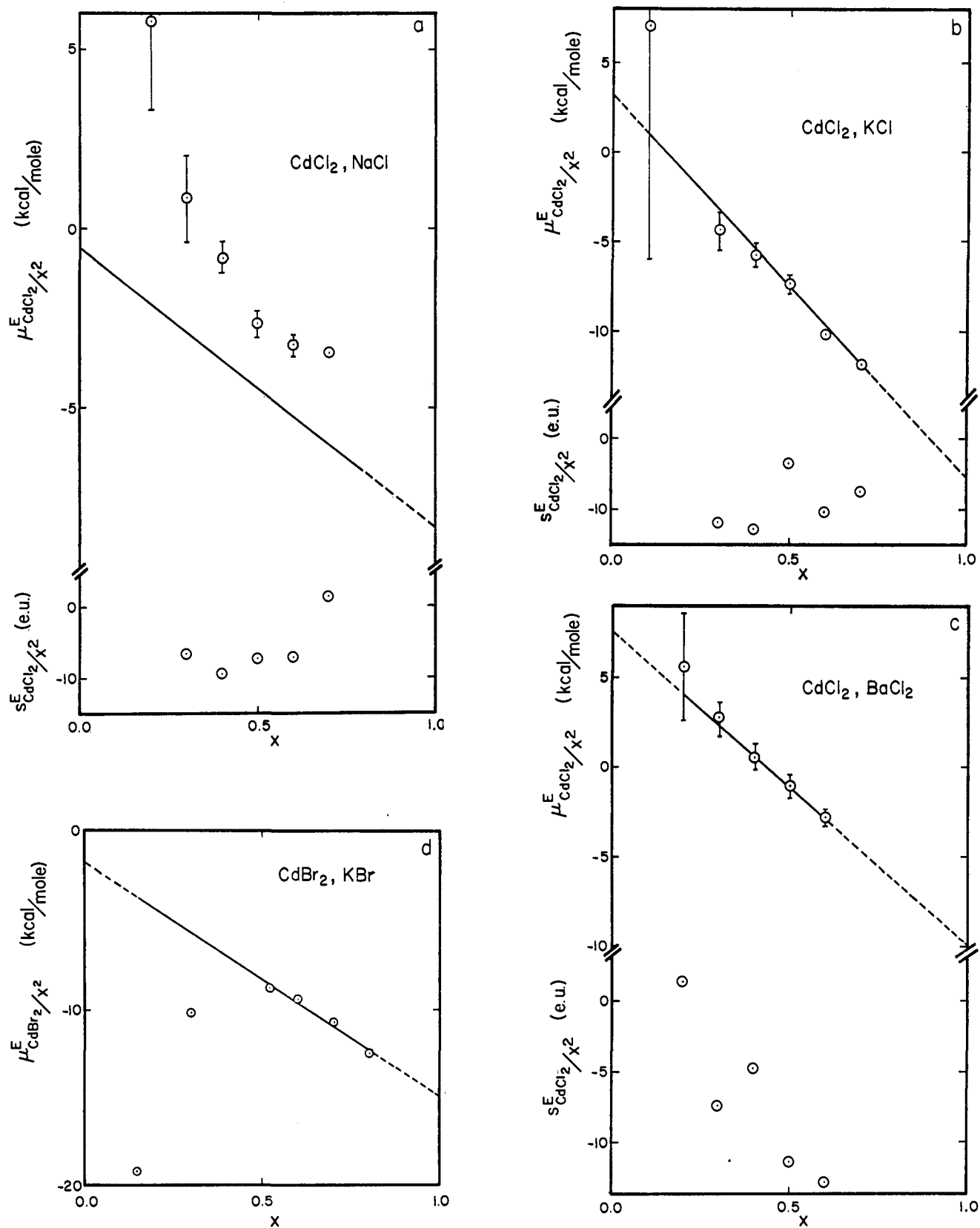
Figure 4.—Experimental values of $\mu^E_{CdCl_2}/x^2$ and $s^E_{CdCl_2}/x^2$ (a-c) in molten binary chloride mixtures (600°). The limits of uncertainty and the solid lines are the result of the present analysis. (a) $CdCl_2(1 - x),NaCl(x)$: ⊙, Lantratov and Alabyshev;[40] - - -, Dijkhuis and Ketelaar.[28,29] (b) $CdCl_2(1 - x),KCl(x)$: Lantratov and Alabyshev.[40] (c) $CdCl_2(1 - x),BaCl_2(x)$: Lantratov and Alabyshev.[40] (d) Experimental values of $\mu^E_{CdBr_2}/x^2$ and $s^E_{CdBr_2}/x^2$ in the molten binary mixture $CdBr_2(1 - x),KBr(x)$ (597.5°): Lantratov and Shevlyakova.[40]

Cl|Cl₂|C cell under equilibrium conditions[62,96] and non-equilibrium conditions.[48,97] The mixture has also been investigated using an emf cell of the type W|Pb|PbCl₂, NaCl|glass|PbCl₂(x = 0.6),NaCl(x = 0.4)|Pb|W,[29] in which the glass is a sodium indicator electrode. The excess free energies calculated from the results of these studies are shown in Figure 8. Inspection shows that all the results confirm that the excess free energy of mixing in this system is small and negative. The equilibrium values of Lantratov and Alabyshev[62] are in good agreement with the values of Dijkhuis and Ketelaar;[29] the nonequilibrium values of Markov, Delimarskii, and Panchenko[48] give a more negative excess free energy; also both nonequilibrium values of Suskii[97] (x = 0.5) and the equilibrium values of Hagemark and Hengstenberg[96] lead to a less negative excess free energy.

The PbCl₂,LiCl mixture has been studied by Lantratov and Alabyshev[62] and by Markov, Delimarskii, and Panchenko;[48] the results for the excess properties are shown in Figure 8b. In line with the evidence from the PbCl₂,NaCl system, the Lantratov and Alabyshev[62] values are recommended as the more reliable.

Hildebrand and Ruhle[47] used a nonequilibrium technique for the study of the PbCl₂,KCl system. Inspection of the derived excess properties (Figure 8c) shows that there is an appreciable difference between these results and those of the more recent studies. It is of interest to note that for this system the non-equilibrium-type studies of Markov, Delimarskii, and Panchenko[48] are in reasonable agreement with the equilibrium data of Lantratov and Alabyshev[62] and Hagemark and Hengstenberg.[96] Reference to Figure 6 shows that the excess entropies from the latter two studies[62,96] are in reasonable agreement, whereas the values based on the earlier study[47] differ significantly.

The results for the PbCl₂,RbCl mixture, calculated from the data of Markov, Delimarskii, and Panchenko[48] (nonequilibrium technique), are illustrated in Figure 8d. In line with the results from this laboratory for the PbCl₂,KCl mixture, it appears that the data for PbCl₂,RbCl may be used for a reasonably sound estimate of the excess free energy.

For PbCl₂,CsCl, the investigation was limited to only two compositions.[96] The excess free energy for this system was derived using these two results and the assumption that the parameter c is zero. It was noted by Hagemark and Hengstenberg[96] that the excess entropy of this mixture is large and positive; this observation may imply that uncertainties are involved in the emf data for this system.

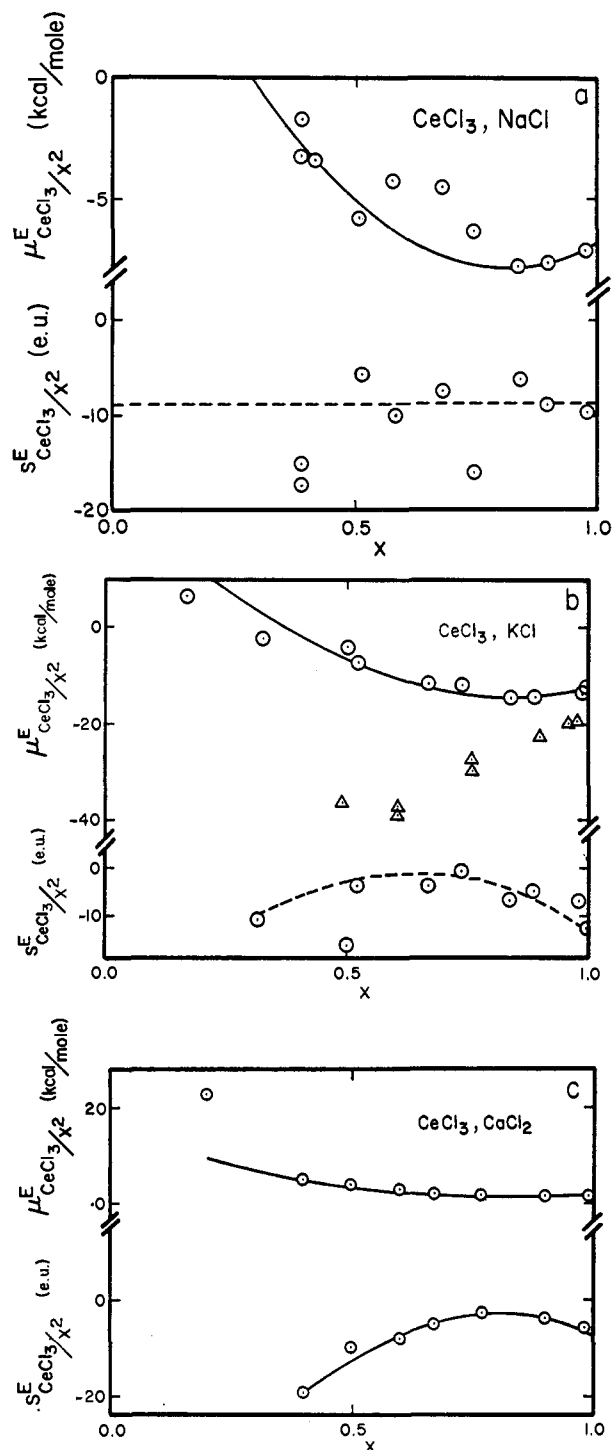The PbCl₂,CaCl₂, PbCl₂,SrCl₂, and PbCl₂,BaCl₂ systems were investigated by Lantratov and Alaby-

(96) K. Hagemark and D. Hengstenberg, private communication, 1967.

(97) L. Suskii, *Zh. Fiz. Khim.*, **30**, 1855 (1956).

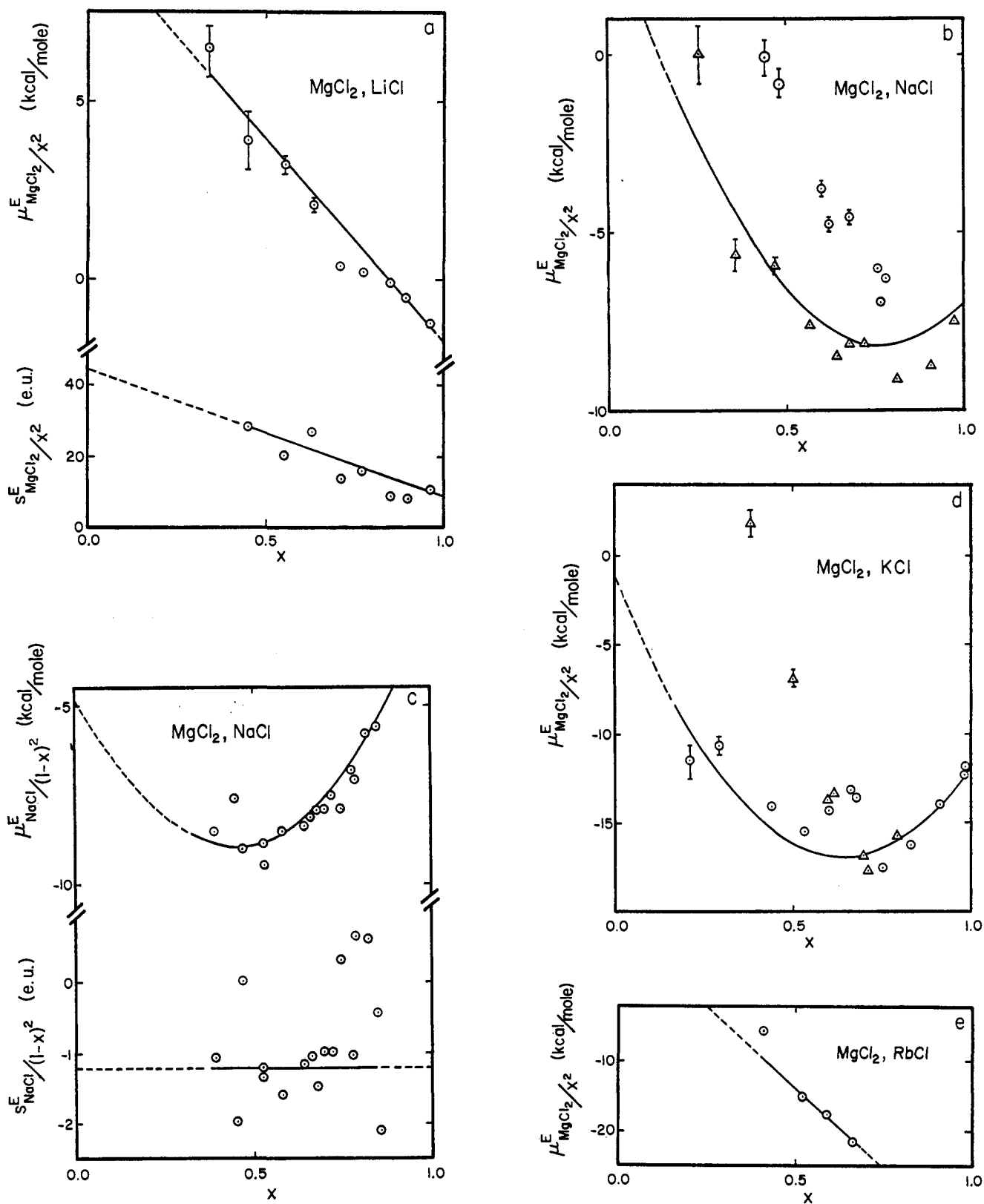Figure 5.—Experimental values of $\mu^E_{CeCl_3}/x^2$ and $s^E_{CeCl_3}/x$ in molten binary chloride mixtures. The solid lines are the result of the present analysis. (a) CeCl₃(1 − x),NaCl(x): ⊙, Senderoff, Mellors, and Bretz,[50] 800°. (b) CeCl₃(1 − x),KCl(x): ⊙, Senderoff, Mellors, and Bretz,[50] 850°; △, Neil,[51] 850°. (c) CeCl₃(1 − x),CaCl₂(x): ⊙, Senderoff, Mellors, and Bretz,[95] 850°.

shev[62] by equilibrium-type cells with lead and chlorine| graphite electrodes. Only two compositions for each mixture appear to have been studied. The excess free energies of these mixtures were calculated as in the

Figure 6.—Experimental values of $\mu^E_{MgCl_2}/x^2$ (or $\mu^E_{NaCl}/(1-x)^2$) and $s^E_{MgCl_2}/x^2$ (or $s^E_{NaCl}/(1-x)^2$) in molten binary chloride mixtures containing $MgCl_2$. The limits of uncertainty and the solid lines are the result of the present analysis. (a) $MgCl_2(1-x),LiCl(x)$: ⊙, Markov, Delimarskii, and Panchenko,[53] 700°. (b) $MgCl_2(1-x),NaCl(x)$: ⊙, Markov, Delimarskii, and Panchenko,[53] 700°; △, Neil, Clark, and Wiswall,[52] 825°. (c) $MgCl_2(1-x),NaCl(x)$: ⊙, Ostvold,[25] 850°. (d) $MgCl_2(1-x),KCl(x)$: ⊙, Markov, Delimarskii, and Panchenko,[53] 700°; △, Neil, Clark, and Wiswall,[52] 800°. (e) $MgCl_2(1-x),RbCl(x)$: ⊙, Markov, Delimarskii, and Panchenko,[53] 700°.

preceding example with the assumption that the parameter c is zero.

The free energy of mixing of the $PbCl_2,ZnCl_2$ mixture was investigated by Wachter and Hildebrand,[63] using an equilibrium cell with lead and chlorine|graphite electrodes. Nakamura and Brenet[64] also studied this system using cells such as $C|Cl_2|PbCl_2|Pb|PbCl_2,Zn-Cl_2|Cl_2|C$. Inspection of Figure 8e shows that the agreement is reasonable between the two studies. The emf data of Nakamura and Brenet[64] were used to generate the excess free energy since cancellation of errors appears more probable in the cell arrangement used by these investigators. For the excess entropies, the data of Wachter and Hildebrand[63] were used since a study of the temperature dependence of the emf appears to have been limited to this one investigation.

Excess free energies of $PbBr_2,NaBr$ mixtures have been determined by Lantratov and Shevlyakova[98] and by Dijkhuis and Ketelaar.[29] Lantratov and Shevlyakova[98] investigated cells as $Pb|PbBr_2,Na-Br|Br_2|C$, but, as noted previously (section II.B), it should be recalled that the $E°$ values differ from the results of Salstrom and Hildebrand[68] and are not in agreement with thermochemical values. The agreement between Lantratov and Shevlyakova[98] excess free energies and values derived from cells in which glass functions as a cation selective membrane[29] $(W|Pb|PbBr_2,NaBr|glass|PbBr_2(x = 0.6),$ $NaBr(x = 0.4)|Br_2.C)$, nevertheless, appears reasonable. This is shown in Figure 9a. This agreement is support for the viewpoint that the results for the $PbBr_2,KBr$ mixtures, also from Lantratov and Shevlyakova,[73] give excess free energies of at least the right order of magnitude. The excess entropies, as determined from the data of these authors, are most likely too high. The results are in Figure 9b.

The $Pb|PbBr_2,ZnBr_2|Br_2|C$ cells were investigated by Salstrom;[69] as noted in section II.B, the values for $E°$ are in good agreement with the thermochemical data. The excess properties calculated from these data are illustrated in Figure 9c. Salstrom reported that Zn metal was observed if the mole fraction of $ZnBr_2$ was greater than 0.8.

The excess free energies at 600° of the PbI_2,NaI mixtures were determined by Dijkhuis and Ketelaar[29] from cells such as $W|Pb|PbI_2,NaI|glass|PbI_2(x = 0.6),NaI(x = 0.4)|Pb|W$ in which the glass is a sodium indicator electrode ($cf.$ section II.C).

7. Mixtures $ZnCl_2,MCl_n$ ($M = Li, Na, K,$ Rb, Cs, Ba)

The difficulties involved with $ZnCl_2$ have been considered elsewhere in this review (section II.A).

(98) M. F. Lantratov and T. N. Shevlyakova, Zh. Neorg. Khim., 6, 192 (1961).
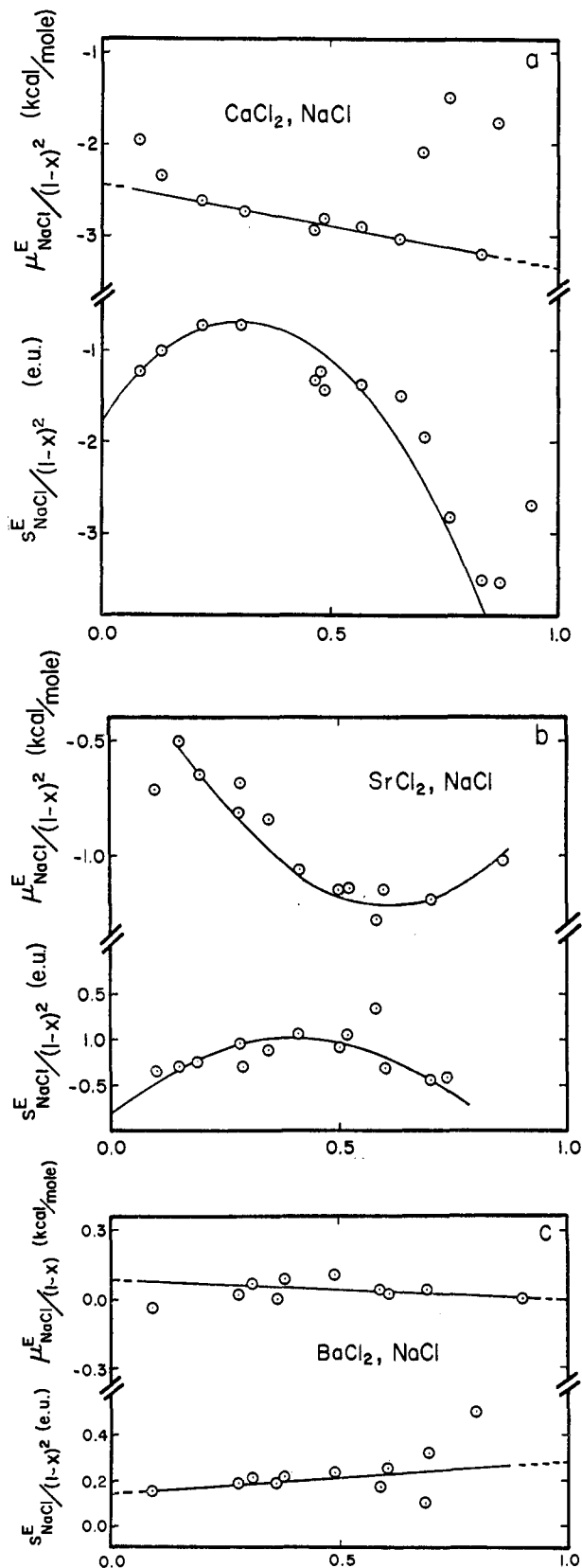

Figure 7.—Experimental values for $\mu^E_{NaCl}/(1 - x)^2$ and $s^E_{NaCl}/(1 - x)^2$ in binary alkaline earth chloride–sodium chloride mixtures. The solid lines are the result of the present analysis: (a) $CaCl_2(1 - x),NaCl(x)$; (b) $SrCl_2(1 - x),NaCl(x)$; (c) $BaCl_2(1 - x),(NaCl(x)$ (all at 850°, Ostvold[25]). Abscissa = x.
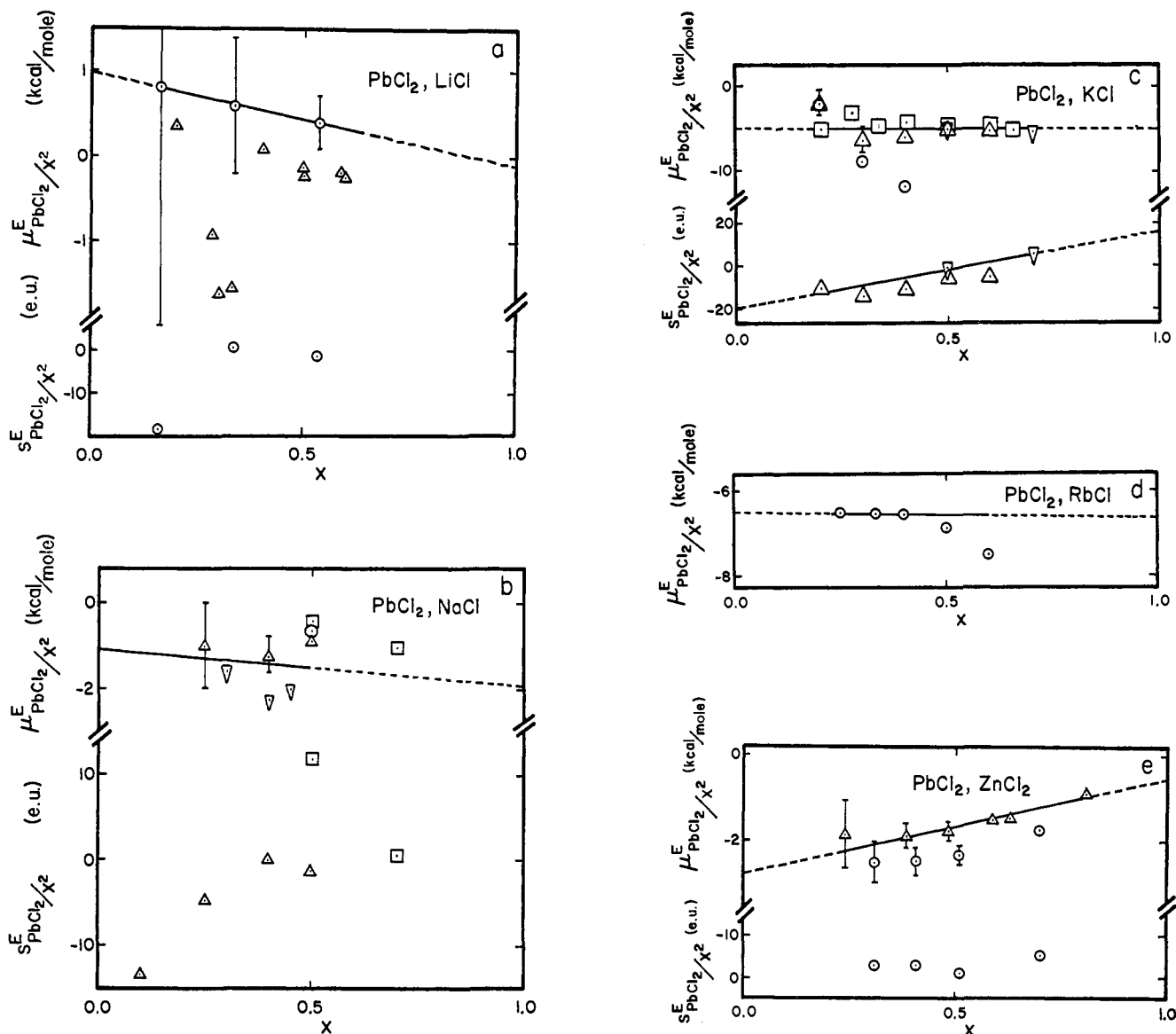
Figure 8.—Experimental values for $\mu^E{}_{PbCl_2}/x^2$ and $s^E{}_{PbCl_2}/x^2$ in binary chloride mixtures. The limits of uncertainty and the solid lines are the result of the present analysis (all data at 600° except where noted). (a) $PbCl_2(1 - x),LiCl(x)$: △, Markov, Delimarskii, and Panchenko;[48] ⊙, Lantratov and Alabyshev.[62] (b) $PbCl_2(1 - x),NaCl(x)$: ▽, Markov, Delimarskii, and Panchenko;[48] △, Lantratov and Alabyshev;[62] ⊙, Suskii;[97] □, Hagemark and Hengstenberg;[96] - - -, Dijkhuis and Ketelaar.[28,29] (c) $PbCl_2(1 - x),KCl(x)$: ⊙, Hildebrand and Ruhle;[47] △, Lantratov and Alabyshev;[62] □, Markov, Delimarskii, and Panchenko;[48] ▽, Hagemark and Hengstenberg.[96] (d) $PbCl_2(1 - x),RbCl(x)$: ⊙, Markov, Delimarskii, and Panchenko.[48] (e) $PbCl_2(1 - x),ZnCl_2(x)$: ⊙, Wachter and Hildebrand,[63] 500°; △, Nakamura and Brenet,[64] 500°.

While uncertainties thus are inherent in free energies of mixtures containing $ZnCl_2$, the results may nevertheless give an approximation of the excess free energies. The $ZnCl_2,LiCl$ mixtures were investigated by Markov and Volkov[66] (nonequilibrium technique). The results are shown in Figure 10. The good agreement between the nonequilibrium values by Markov and Volkov[99] and the equilibrium values of Lantratov and Alabyshev[67] for the $ZnCl_2,KCl$ system (Figure 10c) suggest that the data for $ZnCl_2,LiCl$[66] may be used as a sound first estimate for the excess free energy of this system.

The $ZnCl_2,LiCl$ system was studied by Lantratov and Alabyshev,[67] using equilibrium cells such as $Zn|ZnCl_2,NaCl|Cl_2|C$, and by Dijkhuis and Ketelaar[100] with glass-membrane cells, of the type $W|Zn| ZnCl_2,NaCl|glass|ZnCl_2(x = 0.6),NaCl(x = 0.4)| Zn|W$. It is seen from Figure 10 that excess free energies from these two kinds of emf cells are in good agreement. The excess entropies calculated from the Lantratov and Alabyshev[67] cells appear unrealistic.

Similarly for the $ZnCl_2,KCl$ mixtures, the excess entropies, calculated from the data of Lantratov and

(99) B. F. Markov and S. V. Volkov, *Ukr. Khim. Zh.*, **30**, 545 (1964).

(100) C. G. M. Dijkhuis and J. A. A. Ketelaar, *Electrochim. Acta*, **12**, 795 (1967).
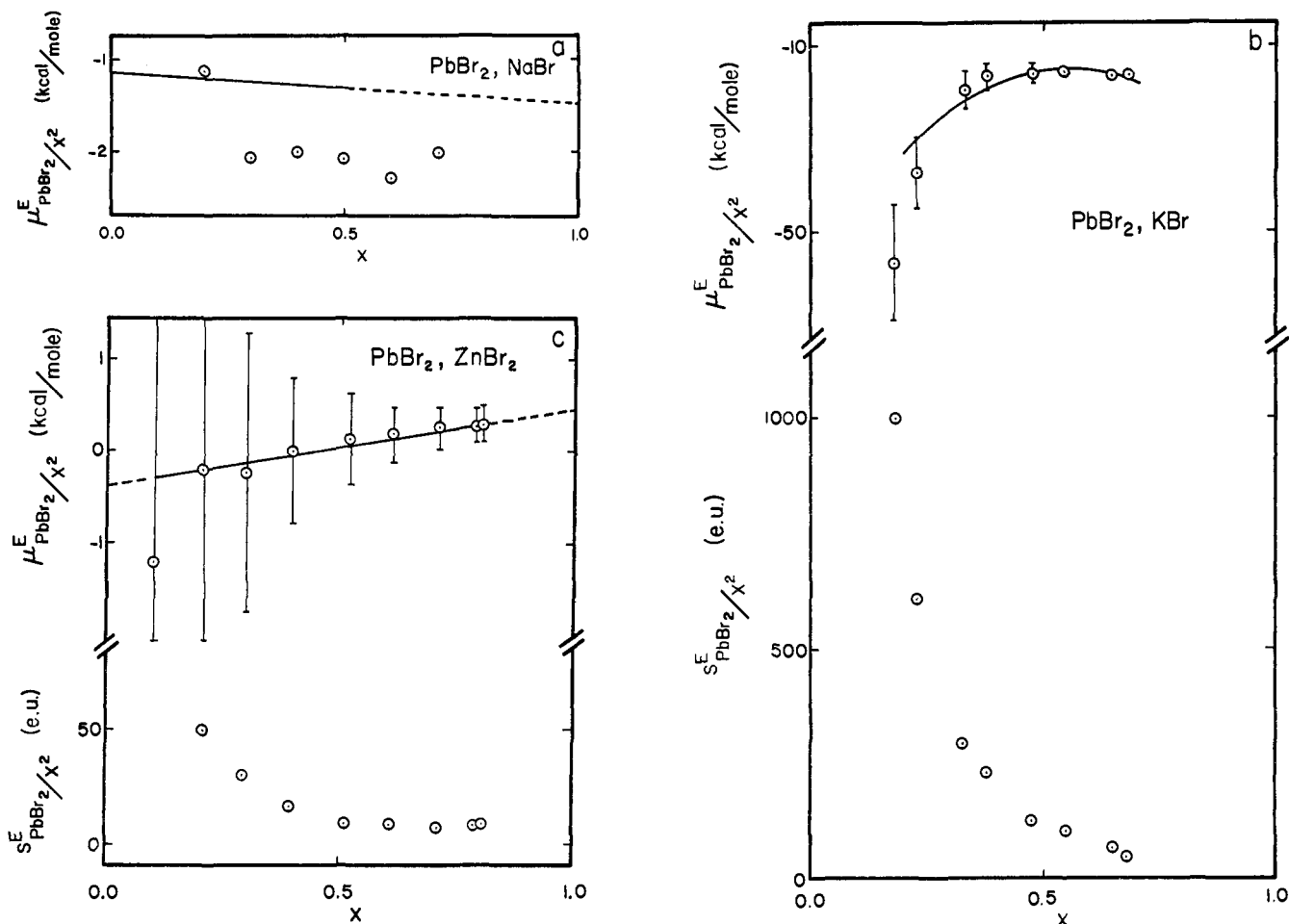
Figure 9.—Experimental values of $\mu^E_{PbBr_2}/x^2$ and $s^E_{PbBr_2}/x^2$ in molten binary bromide mixtures. The limits of uncertainty and the solid lines are the result of the present analysis: (a) $PbBr_2(1 - x)$,$NaBr(x)$, Lantratov and Shevlyakova,[98] 589°; (b) $PbBr_2(1 - x)$, $KBr(x)$, Lantratov and Shevlyakova,[98] 550°; (c) $PbBr_2(1 - x)$,$ZnBr_2(x)$, Salstrom,[69] 500°.

Alabyshev,[67] seem unrealistic (e.g., Figure 10c). For $ZnCl_2$,$RbCl$ mixtures Markov[101] and Markov and Volkov[99] have reported emf data using the nonequilibrium technique. In accord with the quality of the data for the $ZnCl_2$,$LiCl$ system, the results of Markov and Volkov[99] were selected to generate the excess free energies for this mixture. Markov and Volkov,[102] similarly, have determined excess free energies of mixtures $ZnCl_2$,$CsCl$.

The $Zn|ZnCl_2(1 - x)$,$BaCl_2(x)|Cl_2|C$ cells are studied by Lantratov and Alabyshev.[67] These authors report that the excess free energy of the mixture $ZnCl_2$,$BaCl_2$ is negative and less negative than for $ZnCl_2$,$NaCl$ mixtures.

B. MIXTURES WITH A COMMON CATION

The $AgBr$,$AgCl$ mixture was investigated by Murgulescu and Marchidan[70] using cells such as $Ag|AgBr$,$AgCl|Br_2|C$. The $E°$ values are in good agreement with thermochemical data. Thus a systematic error is not involved in the excess free energies derived from the emf data. The $Ag|AgI$,$AgCl|I_2|C$ and $Ag|AgI$,$AgBr|I_2|C$ cells were studied by Sternberg, Adorian, and Galasiu.[76] As already noted (section II.B) the $E°$ values are in reasonable agreement with thermochemical data. The excess properties for these three mixtures are illustrated in Figure 11. Inspection shows that random error in the measurements is relatively small.

The KBr,KCl mixtures were investigated by Ostvold[25] using cells with glass membranes as potassium indicator electrodes (e.g., $C|Br_2|KBr|glass|KBr,KCl|Br_2|C$). The excess properties derived from these data are illustrated in Figure 12a. The same principle was used by Ostvold[25] and by Sternberg and Herdlicka[31] for investigations of the excess properties of the $NaBr$,$NaCl$ system. Ostvold used a specially prepared glass whereas Sternberg and Herdlicka[31] used quartz for the sodium indicator electrode. Figure 12b shows that the two sets of data are in good agreement.

The $PbBr_2$,$PbCl_2$ mixtures were studied by Salstrom and Hildebrand[68] using equilibrium emf techniques.

(101) B. F. Markov, Zh. Fiz. Khim., 31, 2288 (1957).
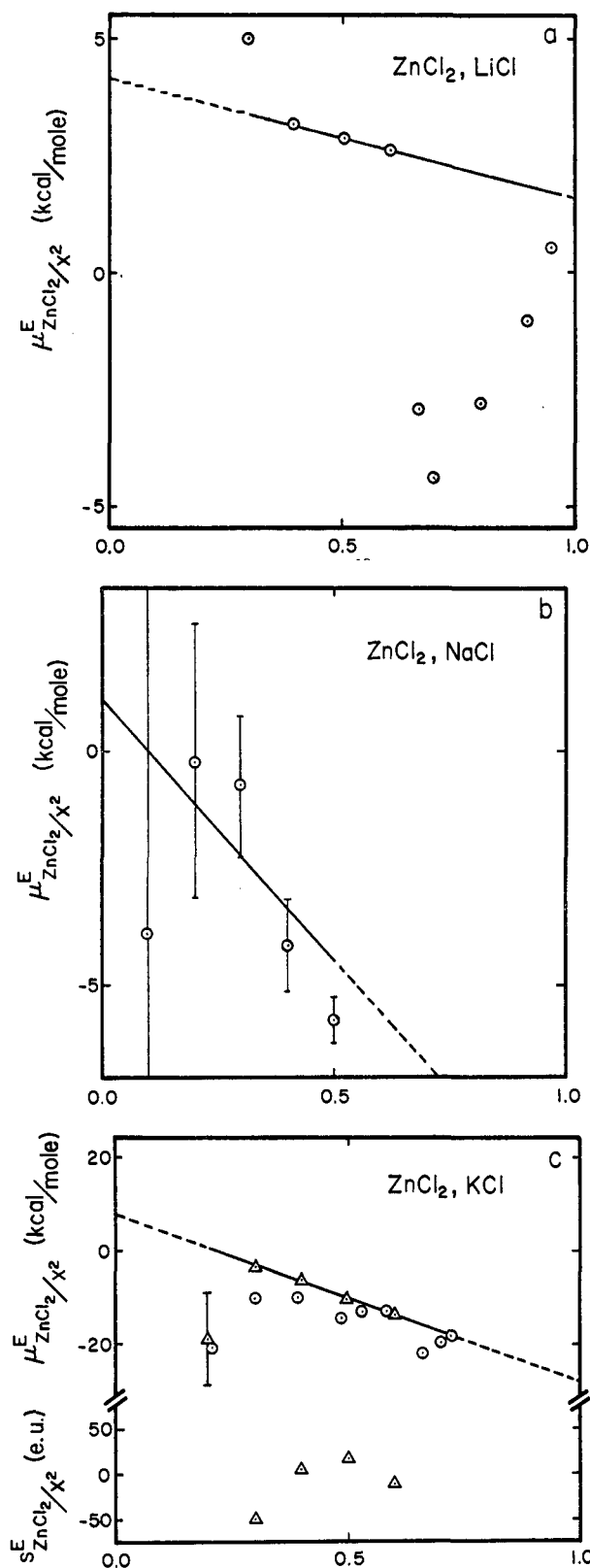(102) B. F. Markov and S. V. Volkov, Ukr. Khim. Zh., 30, 906 (1964).

Figure 10.—Experimental values of $\mu^E_{ZnCl_2}/x^2$ and $s^E_{ZnCl_2}/x^2$ in molten binary chloride mixtures. The limits of uncertainty and the solid lines are the result of the present analysis. (a) $ZnCl_2(1 - x)$,LiCl(x): ⊙, Markov and Volkov,[66] 550°. (b) $ZnCl_2(1 - x)$,NaCl(x): ⊙, Lantratov and Alabyshev;[67] – – –, Dijkhuis and Ketelaar.[29] (c) $ZnCl_2(1 - x)$,KCl(x): ⊙, Markov and Volkov;[99] △, Lantratov and Alabyshev.[67] Abscissa = x.
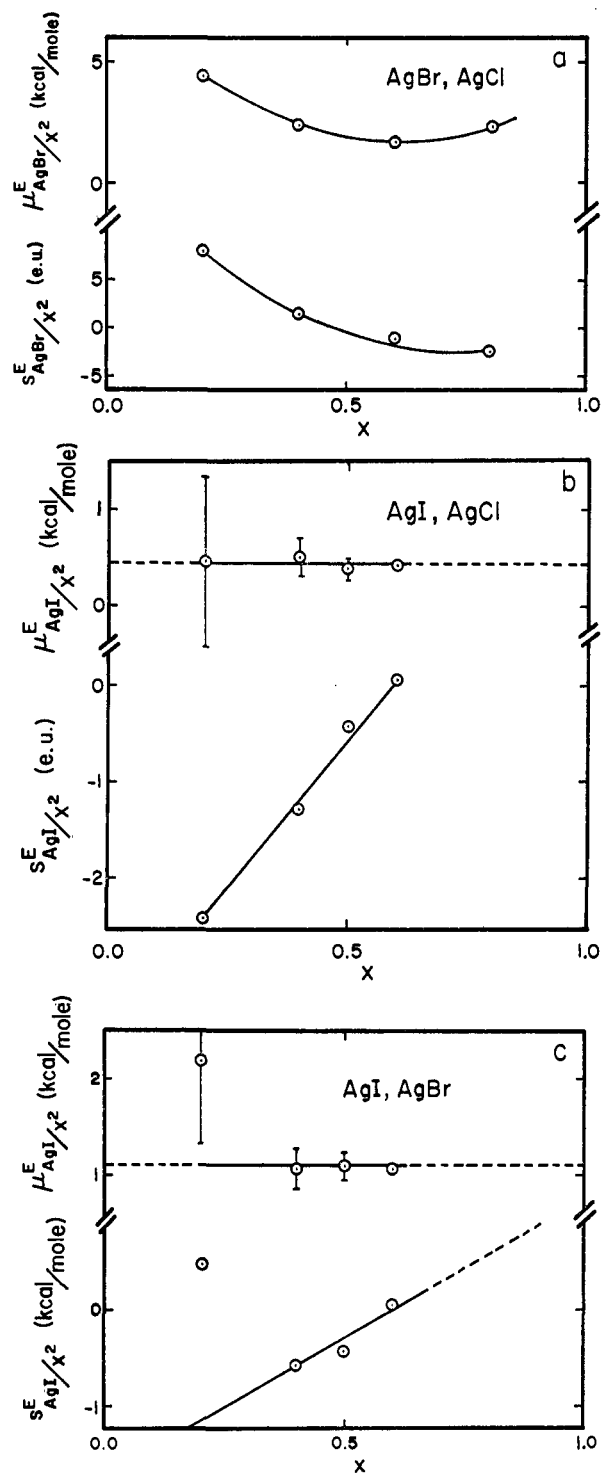
Figure 11.—(a) Experimental values of μ^E_{AgBr}/x^2 and s^E_{AgBr}/x^2 in the molten binary mixture AgBr,AgCl(x). The solid lines are the result of the present analysis, Murgulescu and Marchidan,[70] 600°. (b, c) Experimental values μ^E_{AgI}/x^2 and s^E_{AgI}/x^2 in molten binary mixtures. The solid lines are the result of the present analysis: (b) AgI$(1 - x)$,AgCl(x) and (c) AgI$(1 - x)$, AgBr(x) (Sternberg, Adorian, and Galasiu,[76] both 600°).

The $E°$ was in good agreement with thermochemical data and supports the viewpoint that excess properties derived from these data are of high accuracy. The results are in Figure 13. Only four compositions were

investigated so that the derived excess free energies are somewhat uncertain. The excess entropies, derived from these emf data, do not seem realistic.

V. Results and Discussion

The analysis of equilibrium emf cells after the method outlined in sections III and IV leads to a description of the total excess free energy of mixing (G^E) in terms of a three-parameter equation (i.e., eq 1). Values for the parameters in the expression for the total excess entropy (S^E) can also be gained by this approach (e.g., eq 4). The results for the excess free energy are summarized in Table IV and are illustrated graphically in Figures 14–22. In the latter, values of $G^E/x(1 - x)$ vs. x have been graphed. In-

Figure 12.—(a) Experimental values of $\mu^E{}_{KBr}/x^2$ and $s^E{}_{KBr}/x^2$ in the molten binary mixture KBr$(1 - x)$,KCl(x): Ostvold,[25] 800°. (b) Experimental values of $\mu^E{}_{NaBr}/x^2$ and $s^E{}_{NaBr}/x^2$ in the molten binary mixture NaBr$(1 - x)$,NaCl(x): ○, Ostvold,[25] 800°; △, Sternberg and Herdlicka,[31] 800°.

TABLE IV

VALUES FOR THE PARAMETERS a, b, AND c IN EQUATION FOR THE EXCESS FREE ENERGY OF MIXING

$$G^E = x(1 - x)(a + bx + cx^1)$$

Mixture	Temp, °C	Ref	a, kcal/ mole	b, kcal/ mole	c, kcal/ mole
AgCl,LiCl(x)		87, 88	2.1	0.0	0.0
AgCl,NaCl(x)		37, 89, 90	0.8	0.0	0.0
AgCl,KCl(x)	650	39, 43	−1.5	0.4	0.0
AgCl,PbCl₂(x)	550	42	−0.15	0.2	0.0
CdCl₂,NaCl(x)	600	28, 29, 40	−4.45	−3.85	0.0
CdCl₂,KCl(x)	600	40	−7.5	−10.7	0.0
CdCl₂,BaCl₂(x)	600	40	−1.0	−8.8	0.0
CeCl₃,NaCl(x)	800	50	−2.7	−13.6	9.3
CeCl₃,KCl(x)	850	50, 51	−1.87	−31.75	20.48
CeCl₃,CaCl₂(x)	850	95	4.80	−8.79	5.37
MgCl₂,LiCl(x)	700	53	3.95	−5.75	0.00
MgCl₂,NaCl(x)		25, 51–53	−4.80	−9.39	7.08
MgCl₂,KCl(x)	800	51–53	−12.84	−11.88	12.96
CaCl₂,NaCl(x)	850	25	−2.45	−0.45	0.00
SrCl₂,NaCl(x)	850	25	−0.02	−1.92	1.03
BaCl₂,NaCl(x)	850	25	0.08	−0.04	0.00
PbCl₂,LiCl(x)	600	48, 62	0.45	−0.55	0.00
PbCl₂,NaCl(x)	600	28, 29, 48, 62, 96, 97	−1.52	−0.39	0.00
PbCl₂,KCl(x)	600	47, 48, 62, 96	−5.0	0.0	0.0
PbCl₂,RbCl(x)	600	48	−6.5	0.0	0.0
PbCl₂,CsCl(x)	650	96	−7.3	−5.2	0.0
PbCl₂,CaCl₂(x)	650	62	0.6	−2.8	0.0
PbCl₂,SrCl₂(x)	650	62	1.3	−1.6	0.0
PbCl₂,BaCl₂(x)	650	62	−0.7	−3.0	0.0
PbCl₂,ZnCl₂(x)	500	63, 64	−1.65	1.15	0.0
ZnCl₂,LiCl(x)	550	66	2.9	−1.3	0.0
ZnCl₂,NaCl(x)	600	29, 67	−4.37	−5.54	0.00
ZnCl₂,KCl(x)	550	67, 99	−10	−18	0
ZnCl₂,BaCl₂		67	$0 \geqq a \geqq -4$		
AgBr,LiBr(x)	550	72	1.8	0.0	0.0
AgBr,NaBr(x)	600	91	1.05	0.0	0.0
AgBr,KBr(x)	600	92	−1.45	−0.30	0.0
AgBr,RbBr(x)	550	93	−2.6	0.0	0.0
AgBr,PbBr₂(x)	550	94	0.05	0.15	0.0
CdBr₂,KBr(x)	597.5	73	−8.3	−6.6	0.0
PbBr₂,NaBr(x)	589	98	−1.31	−0.16	0.0
PbBr₂,KBr(x)	550	98a	−27.5	32.5	−50.0
PbBr₂,ZnBr₂(x)	500	69	0.05	0.40	0.00
AgI,KI(x)	600	75	−1.95	1.20	0.1
CdI₂,NaI	600	28, 29	−2.28	−1.89	0.0
PbI₂,NaI	600	28, 29	−0.46	−0.14	0.0
AgBr,AgCl(x)	600	70	3.25	−4.43	5.22
AgI,AgCl(x)	600	76	0.45	0.00	0.00
AgI,AgBr(x)	600	76	1.15	0.00	0.00
KBr,KCl(x)	800	25	0.50	−0.55	0.00
NaBr,NaCl(x)	800	25, 31	0.40	−0.10	0.00
PbBr₂,PbCl₂(x)	500	68	−2.6	0.0	0.0

spection of eq 1 shows this to be a sensitive method for investigating the asymmetry of the excess energy relative to composition dependence in a normal mole fraction. The description of the total excess properties in this manner was first advanced by Kleppa and Hersh[103] and by Kleppa, Clarke, and Hersh[104] for the heats of mixing of binary nitrate mixtures. The theoretical significance of the a, b, and c parameters in the expression for the total heats of mixing has been interpreted from the conformal solution theory for ionic mixtures by Reiss, Katz, and Kleppa,[10] Blander,[11] Davis and Rice,[105] and Davis.[106] No similar theoretical treatment exists for the excess free energies of mixing. A difficulty in interrelating the results of heats of mixing to the expressions for excess free energies is the lack of information on the excess entropy of mixing. This

(103) O. J. Kleppa and L. S. Hersh, J. Chem. Phys., 34, 351 (1961).

(104) O. J. Kleppa, R. B. Clarke, and L. S. Hersh, ibid., 35, 175 (1961).

(105) H. T. Davis and S. A. Rice, ibid., 41, 14 (1964).
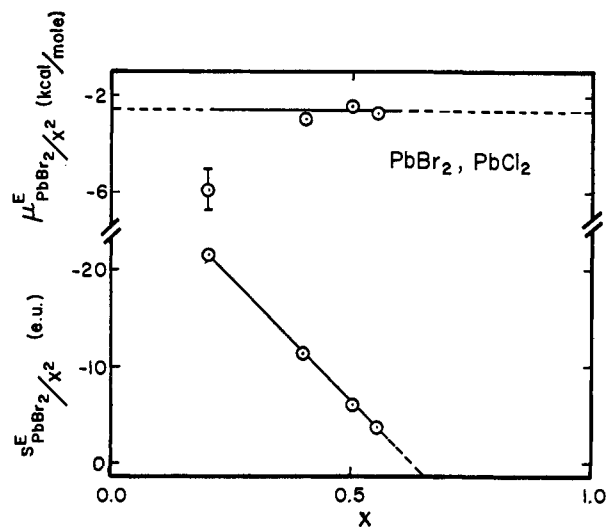
(106) H. T. Davis, ibid., 41, 2761 (1964).

Figure 13.—Experimental values of $\mu^E_{PbBr_2}/x^2$ and $s^E_{PbBr_2}/x^2$ in the molten binary mixture $PbBr_2(1 - x),PbCl_2(x)$: Salstrom and Hildebrand,[68] 500°.
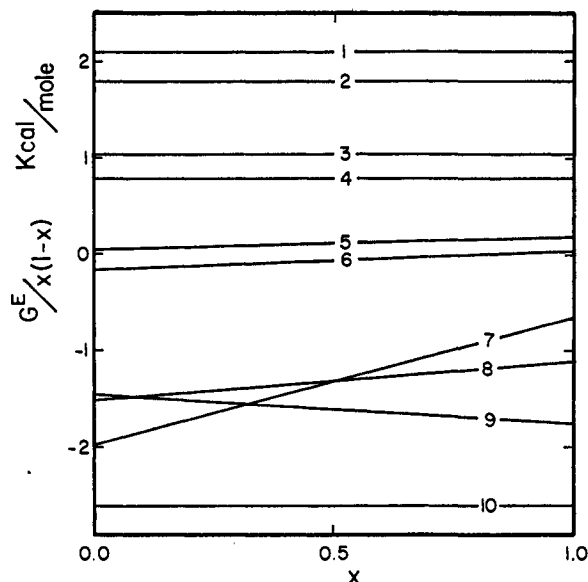

Figure 14.—Plots of $G^E/x(1 - x)$ vs. x for binary molten salt mixtures with a common halide ion and with silver as a constituent ion (Table IV): (1) (Ag,Li)Cl, (2) (Ag,Li)Br, (3) (Ag,Na)Br, (4) (Ag,Na)Cl, (5) (Ag,Pb)Br, (6) (Ag,Pb)Cl, (7) (Ag,K)I, (8) (Ag,K)Cl, (9) (Ag,K)Br, (10) (Ag,Rb)Br.

problem has been discussed and summarized by Ostvold[25] and by Forland.[6] Kleppa and McCarty[107] noted a parallel between the excess entropy and excess volumes, whereas Forland[6] calculated excess entropies from lattice models, assuming nonrandom mixing of ions. The difficulties in predicting excess entropies are illustrated by the fact that different signs for heat of mixing and excess entropy of mixing have been reported,[21,28,29,107] whereas existing theoretical approaches predict that these two quantities should be of the same

sign. Because of the lack of information in this area, the discussion of the results in Table IV and Figures 14-22 will be limited to qualitative considerations.

The excess free energies of (silver,alkali) halide mixtures and (silver,lead) halide mixtures are illustrated in Figure 14. Inspection shows that pairs of cations determine the order of magnitude of the excess free energy. A variation of the kind of anion has only a minor influence. Furthermore, the excess free energy becomes more negative in the sequence (Ag,Li)X, (Ag,Na)X, (Ag,K)X, (Ag,Rb)X (X = Cl⁻ or Br⁻), whereas the excess free energy of the Pb^{2+}-containing melts is nearly zero. It is also evident that most of these mixtures have an excess free energy, which, in first approximation, is symmetrical in mole fraction. However, because of experimental reasons (section IV), no conclusive regularities can be established for these asymmetries.

A comparison of these excess free energies (Figure 14) with excess free energies of (cadmium,alkali) halide mixtures (Figure 15) shows that the absolute value of excess free energies for the last-mentioned mixtures is much higher. Here it is again apparent that the K^+-containing melt has a more negative excess free energy than the Na^+-containing melt. Although more experimental results are needed, the results indicate a regular trend; namely, the excess free energy becomes more negative as one passes from iodide to bromide to chloride.

Mixtures containing $CeCl_3$ and $MgCl_2$ are strongly interacting and have excess free energies for which the parameter c (eq 1) has a significant value (Figures 16 and 17).

The excess free energy of the $CeCl_3,CaCl_2$ mixture is positive; the $CeCl_3,NaCl$ system has a negative excess free energy; and the excess free energy of the $CeCl_3,KCl$ mixture is even more negative. The same sequence is apparent relative to the influence of alkali ions on the excess free energy in the $MgCl_2$-containing melts (Figure 17). In the (alkaline earth,sodium) chloride mixtures the excess free energy is small. The (Ba,Na)-Cl system has a nearly zero excess free energy, whereas (Sr,Na)Cl and (Ca,Na)Cl have somewhat negative excess free energies.

The excess free energy for (lead,alkali) chloride mixtures is illustrated in Figure 18. Inspection of this figure shows that the excess free energy becomes more negative when going from (Li,Pb)Cl to (Na,Pb)Cl and (Rb,Pb)Cl, and to (Cs,Pb)Cl. That this regularity is not observed in the series (Pb,Sr)Cl, (Pb,Ca)-Cl, and (Pb,Ba)Cl is possibly due to the experimental uncertainties. By comparing the (Pb,Zn)Cl and (Pb,Zn)Br mixtures it is again apparent that the excess free energy of the chloride mixture is more negative than the excess free energy of the bromide mixture. The values for the parameter a in the series of mixtures

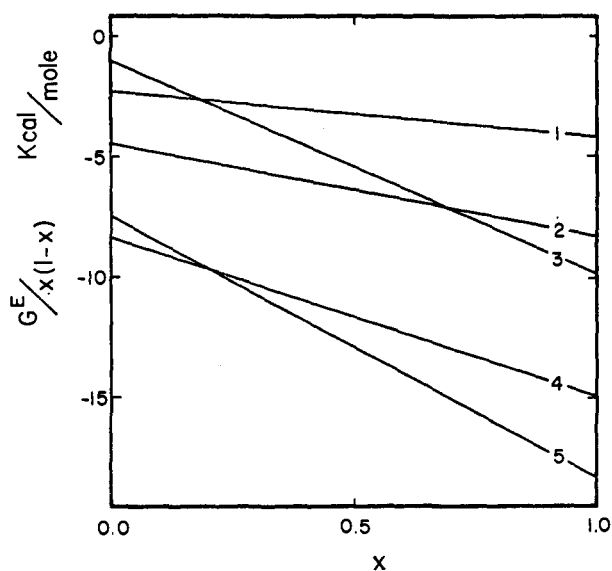(107) O. J. Kleppa and F. G. McCarty, J. Phys. Chem., 68, 3846 (1964).

‾ Figure 15.—Plots of $G^E/x(1 - x)$ vs. x for binary molten salt mixtures with a common halide ion and with cadmium as a constituent ion (Table IV): (1) (Cd,Na)I, (2) (Cd,Na)Cl, (3) (Cd,Ba)Cl, (4) (Cd,K)Br, (5) (Cd,K)Cl.
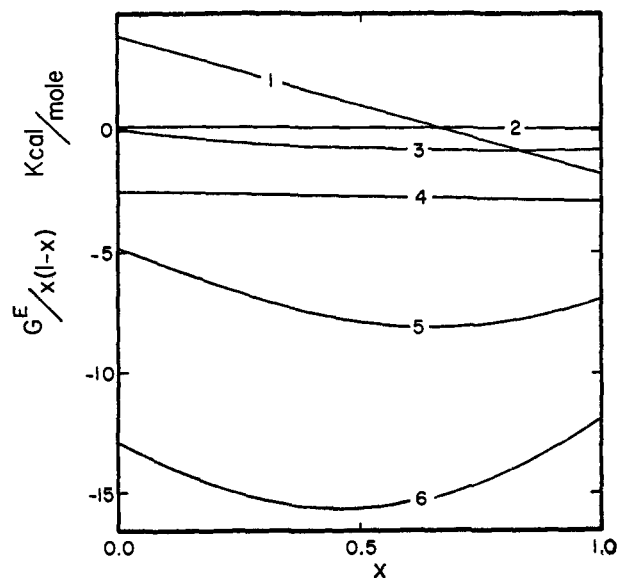
Figure 17.—Plots of $G^E/x(1 - x)$ vs. x for binary molten chloride mixtures containing Mg, Ba, Sr, or Ca as constituent ion (Table IV): (1) (Mg,Li)Cl, (2) (Ba,Na)Cl, (3) (Sr,Na)Cl, (4) (Ca,Na)Cl, (5) (Mg,Na)Cl, (6) (Mg,K)Cl.
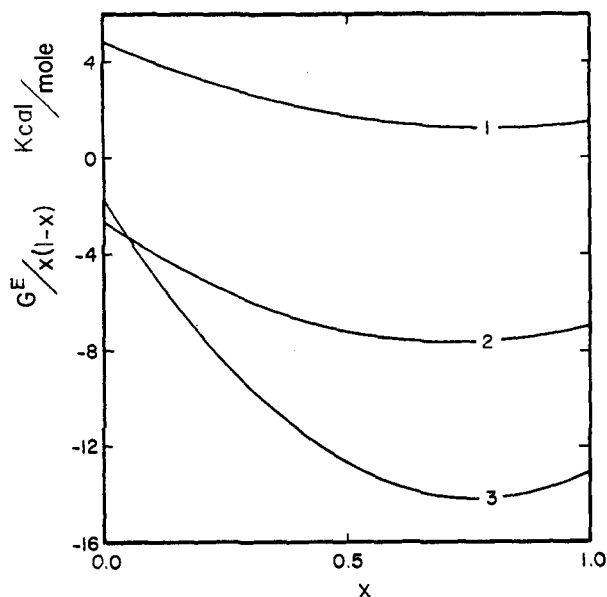

Figure 16.—Plots of $G^E/x(1 - x)$ vs. x for binary molten chloride mixtures containing cerium as constituent ion (Table IV): (1) (Ce,Ca)Cl, (2) (Ce,Na)Cl, (3) (Ce,K)Cl.
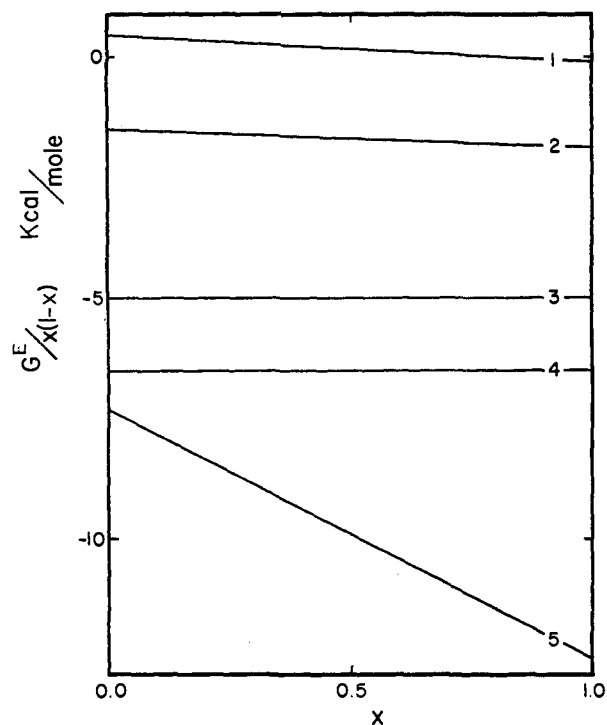
Figure 18.—Plots of $G^E/x(1 - x)$ vs. x for binary molten (lead,alkali) chloride mixtures (Table IV): (1) (Pb,Li)Cl, (2) (Pb,Na)Cl, (3) (Pb,K)Cl, (4) (Pb,Rb)Cl, (5) (Pb,Cs)Cl.

(Pb,Na)Cl, (Pb,Na)Br, and (Pb,Na)I are, respectively, −1.52, −1.31, and −0.46 kcal/mole (Table IV and Figure 19); i.e., the chloride mixture has the most negative excess free energy. In Figure 20 it is seen that a large and negative value is found for the excess free energy of the PbBr$_2$,KBr mixture. It is likely that the experimental uncertainties contribute to this result.

As noted elsewhere (section IV) the determination of excess free energies of ZnCl$_2$-containing melts by formation cells, using the chlorine electrode, gives rise to systematic errors. The excess free energies de-

termined in this manner are illustrated in Figure 21. Only the ZnCl$_2$,NaCl mixture was investigated by equilibrium emf cells. Considering the experimental uncertainties, it is remarkable that the trend, noted in other mixtures, is also evident here; i.e., the excess free energy becomes more negative in the sequence (Zn,Li)Cl, (Zn,Na)Cl, (Zn,K)Cl, (Zn,Rb)Cl. The
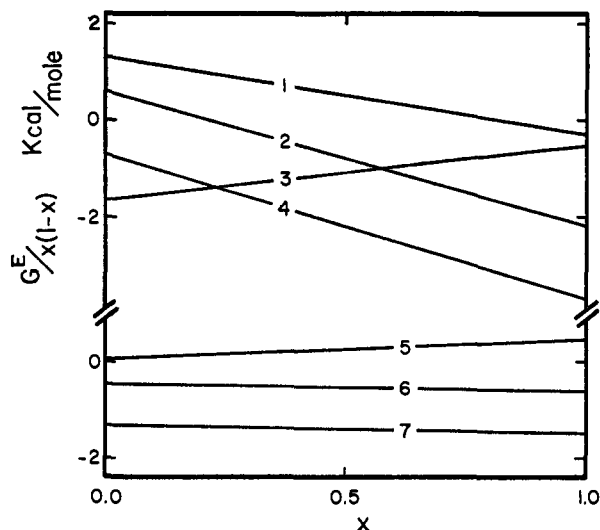
Figure 19.—Plots of $G^E/x(1 - x)$ vs. x for binary molten halide mixtures with lead as constituent ion (Table IV): (1) (Pb,Sr)Cl, (2) (Pb,Ca)Cl, (3) (Pb,Zn)Cl, (4) (Pb,Ba)Cl, (5) (Pb,Zn)Br, (6) (Pb,Na)I, (7) (Pb,Na)Br.
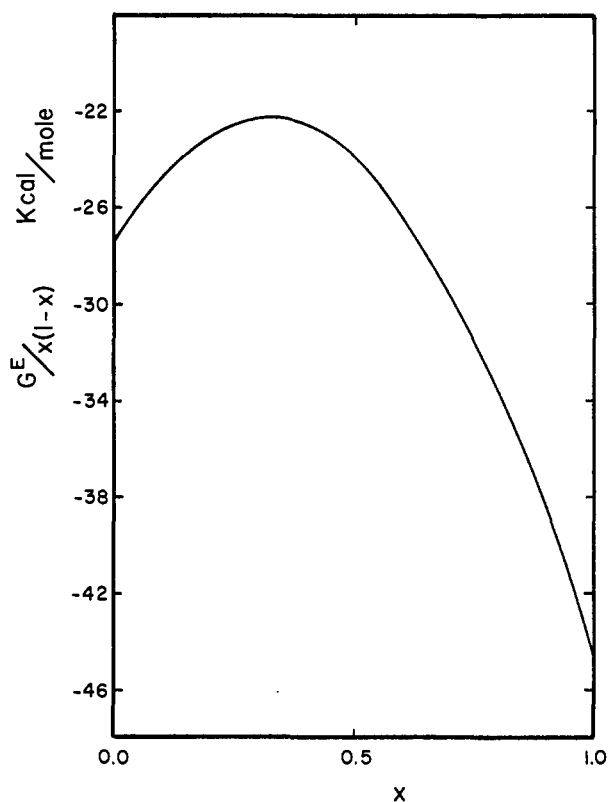

Figure 20.—Plot of $G^E/x(1 - x)$ vs. x for the molten binary mixture PbBr₂,KBr (Table IV).

mixture (Zn,Cs)Cl seems to be an exception. Realizing the significant experimental uncertainties involved in the latter system, it is not improbable that this exception is due to experimental reasons.

The excess free energies of binary mixtures with a common cation are summarized in Figure 22. Inspection shows clearly that more experimental data are
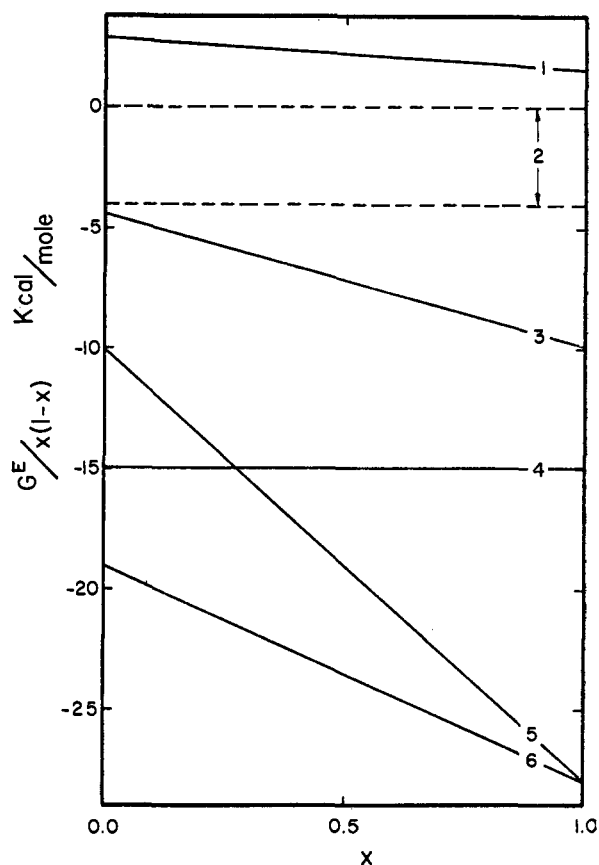
Figure 21.—Plot of $G^E/x(1 - x)$ vs. x for molten binary chloride mixtures with zinc as constituent ion (Table IV): (1) (Zn,Li)Cl, (2) (Zn,Ba)Cl, (3) (Zn,Na)Cl, (4) (Zn,Cs)Cl, (5) (Zn,K)Cl, (6) (Zn,Rb)Cl.

needed before even qualitative rules can be advanced for this class of mixtures. With the exception of the Pb(Br,Cl) mixture, the excess free energies are nearly zero [Ag(I,Cl), Na(Br,Cl), K(Br,Cl)] or are positive [Ag(Br,Cl), Ag(I,Br)]. The fact that the values for Ag(Br,Cl) are more positive than for Ag(I,Br) seems intuitively incorrect.

It was shown elsewhere (section III) that the values of the excess entropies can be gained from the temperature dependence of the emf data. Another approach is from excess free energy and heats of mixing data, according to the well-known relation

$$G^E = H^E - TS^E \qquad (17)$$

A comparison of the results gained by these two methods is illustrated in Figure 23 for the systems AgCl,LiCl and AgCl,NaCl. The solid lines in these figures are the calculated results using the temperature dependence of the emf data of formation cells. The points on the graph are based on the use of the heats of mixing data by Hersh and Kleppa[108] and the excess free energies

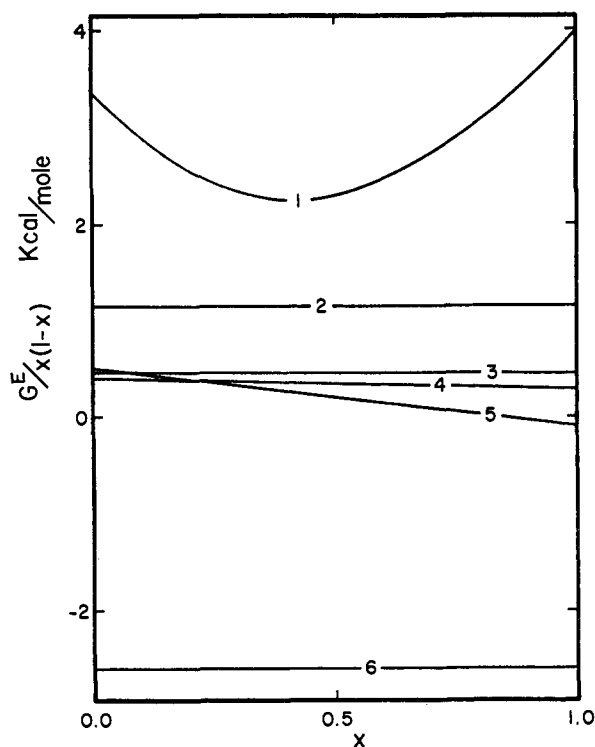(108) L. S. Hersh and O. J. Kleppa, J. Chem. Phys., 42, 1309 (1965).

Figure 22.—Plots of $G^E/x(1 - x)$ vs. x for binary molten mixtures with Ag, Na, K, or Pb as common cation: (1) Ag(Br,Cl), (2) Ag(I,Br), (3) Ag(I,Cl), (4) Na(Br,Cl), (5) K(Br,Cl), (6) Pb(Br,Cl).

Figure 23.—Comparison of excess entropies determined by combining heats of mixing (H^E) and excess free energies (G^E) or determined from the temperature dependence of emf's: ○, $H^E/x(1 - x)$; ●, $TS^E/x(1 - x)$ determined by combining G^E and H^E. The solid lines are values for $G^E/x(1 - x)$ or $TS^E/x(1 - x)$ as determined from emf values.

calculated from the formation cell emf data. It is clearly evident that, if the emf values and the temperature dependence of these data are known with high accuracy, the excess entropies can be calculated with quite reasonable certainty.

VI. CONCLUSIONS

The analysis of emf data of equilibrium-type cells with binary molten salt mixtures having a common ion as liquid electrolyte shows clearly that the absolute values of the excess free energies in these mixtures are small compared with the total "lattice" energy. Although the absolute values for the excess free energies are small, there are some regularities between various kinds of mixtures and their excess free energy. There is a need for additional studies in order to firm up the observed trends in the excess energies as well-defined "rules."

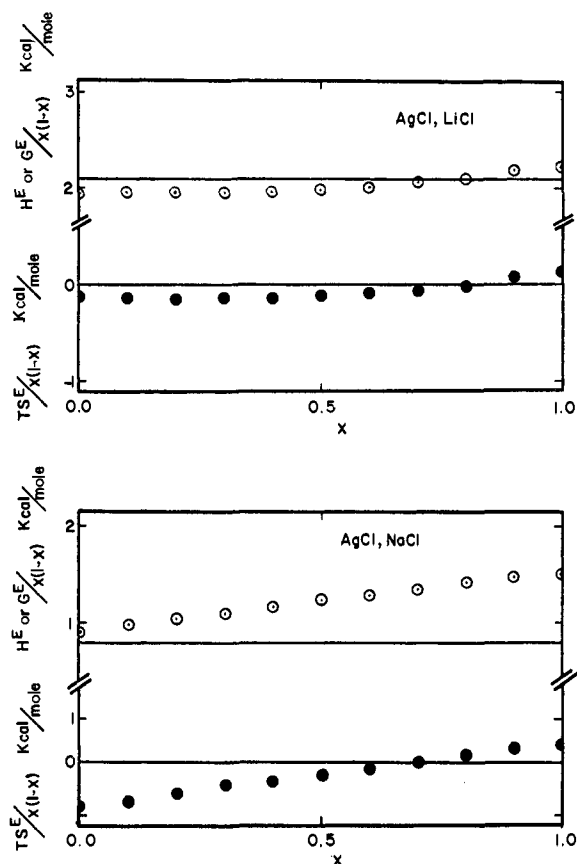The usefulness of excess free energies for the evaluation of the structure and properties of molten salts is limited largely by the lack of information on excess entropies. Heats of mixing from calorimetric measurements and studies of the emf of equilibrium cells over a temperature range are important for advances in this area.