

Table II. Analysis of the Copper Hyperfine and  $g$  Tensors

	$\text{Cu}_x\text{Zn}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$	$\text{Cu}_x\text{Cd}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$
Case I ( $A_x, A_y < 0; A_z > 0$ )		
$\kappa$	0.322	0.301
$\alpha$	0.875	0.877
$\beta$	0.201	0.176
$\alpha^2$	0.765	0.770
$\beta^2$	0.040	0.031
Case II ( $A_x < 0; A_y, A_z > 0$ )		
$\kappa$	0.301	0.274
$\alpha$	0.839	0.838
$\beta$	0.389	0.362
$\alpha^2$	0.704	0.702
$\beta^2$	0.151	0.131

copper ion ( $\alpha^2$ ) is calculated to be 0.76 (case I) or 0.70 (case II) while the total density on the three nitrogen atoms is computed to be 0.26. If these values are reasonably correct, the results suggest that the extent of delocalization of the unpaired electron onto the oxygen atoms of the nitrate ions is small (case II) or insignificant (case I), since the three nitrogen atoms and the copper ion account for essentially all of the electron density. Unfortunately,  $^{16}\text{O}$  has no nuclear spin; therefore, one cannot obtain an experimental measure of the spin density on the oxygen atoms. It should be mentioned that Smith has recently criticized the use of epr constants,  $g$  values specifically, for the calculation of the molecular orbital parameters of copper(II) complexes.<sup>23</sup> While he specifically discussed tetragonal complexes, the criticisms undoubtedly apply to copper(II) complexes of other geometries as well. Although the present study makes use of the ligand and copper hyperfine constants in addition to the  $g$  values, it is probably unwise to expect the molecular orbital parameters which have been derived to be more than qualitatively accurate.

There are some small but significant differences in the spectral parameters of the copper complex obtained from the two different host lattices. The analysis of the copper hyperfine and  $g$  tensors indicates that the amount of  $d_{x^2-y^2}$  orbital mixed into the unpaired electron's wave function ( $\beta$ ) is somewhat smaller in the cadmium lattice (both case I and case II).

(23) D. W. Smith, *J. Chem. Soc. A*, 3108 (1970).

Table III. Analysis of Ligand Hyperfine Constants

	$\text{Cu}_x\text{Zn}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$	$\text{Cu}_x\text{Cd}_{1-x}$ $(\text{py})_3(\text{NO}_3)_2$
N(1): $\gamma^2 = K/513, \epsilon^2 = (T - 0.165)/16.9$		
$K, \times 10^{-4} \text{ cm}^{-1}$	10.5	9.6
$T, \times 10^{-4} \text{ cm}^{-1}$	1.20	1.20
$\gamma^2$	0.020	0.018
$\epsilon^2$	0.061	0.061
N(2) and N(2'): $\gamma^2 = K/513, \epsilon^2 = (T - 0.173)/16.9$		
$K, \times 10^{-4} \text{ cm}^{-1}$	12.4	12.3
$T, \times 10^{-4} \text{ cm}^{-1}$	1.32	1.35
$\gamma^2$	0.024	0.024
$\epsilon^2$	0.068	0.070

According to our previous argument, a decrease in  $\beta$  would indicate a reduction in electron density along the  $y$  axis of the molecule. This supposition is supported by the fact that the coupling constants for N(1), which lies along the  $y$  axis, are about 10% smaller in the copper-doped cadmium lattice than in the zinc lattice. The differences in spectral parameters for the two lattices indicate that the molecular structure of the copper complex is at least somewhat affected by the host lattice. Unfortunately, the estimation of the amount of structural change necessary to account for the observed differences in spectra is a very difficult problem.

On the whole, this spectral analysis has given an internally consistent and physically reasonable description of the ground-state electronic structure of the dinitratotris(pyridine)copper(II) complex. The inability to determine with certainty the relative signs of the copper hyperfine constants (cases I and II) is an obvious weakness of this treatment, but fortunately the same physical picture results in both cases. It appears that a highly distorted octahedron is a very plausible description of the coordination sphere of dinitratotris(pyridine)-copper(II).

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**Registry No.**  $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ , 49664-79-1;  $\text{Zn}(\text{py})_3(\text{NO}_3)_2$ , 32124-88-2;  $\text{Cd}(\text{py})_3(\text{NO}_3)_2$ , 49564-51-4.

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## Binary Silver Bromide-Alkali Bromide Melts. Calculated and Measured Energies of Mixing

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Excess Gibbs free energies of mixing, calculated using the Davis-Rice theory, for silver bromide-alkali bromide melts are found to agree with the experimental values. Precise measurements of energies of mixing for the  $\text{AgBr-ABr}$  ( $A = \text{Li, Na, K, Rb, Cs}$ ) systems are presented which also enable, for the first time, satisfactory theoretical predictions of excess entropies of mixing to be made. The excess entropies of mixing are such that  $\Delta G^E$  cannot be approximated by  $\Delta H^M$  as usually assumed, especially for  $\text{AgBr-LiBr}$ . The importance of a silver-graphite thermocouple emf correction is explained and the Pelton-Flengas theory is tested.

### Introduction

As outlined in a preliminary communication,<sup>1</sup> measurements

(1) R. L. Paul and H. C. Brookes, *Inorg. Nucl. Chem. Lett.*, **8**, 629 (1972).

of energies of mixing of molten  $\text{AgBr-ABr}$  ( $A = \text{Na, K, Rb, Cs}$ ) systems have been obtained using emf formation cells. The  $\text{AgBr-LiBr}$  system, which displays a large negative excess entropy of mixing, has since been investigated in our labora-

tory. Efforts to predict enthalpies of mixing by calculations using the Davis-Rice (DR) theory,<sup>2</sup> which is an extension of conformal solution theory, were unsuccessful<sup>3</sup> particularly for AgBr-LiBr because it was assumed that  $T\Delta S^E$  was negligibly small. No values of  $\Delta S^E$  were previously available to test this, but our results indicate that the above assumption explains the 1200-cal discrepancy between the heats of mixing for AgBr-LiBr measured by Hersh, *et al.*,<sup>3</sup> and those calculated from the DR theory. This paper presents the first precise measurements of  $\Delta S^E$  for the AgBr-ABr (A = Li, Na, K, Rb, Cs) molten systems, and these values together with the excess free energies of mixing,  $\Delta G^E$ , have been successfully interpreted using a simple extension of existing theories.

### Experimental Section

**Reagents.** Silver bromide and lithium bromide (Research Organic/Inorganic Chemical Corp., 99.9%), sodium bromide, potassium bromide, and cesium bromide (British Drug Houses Ltd., 99.9%), and rubidium bromide (Ventron Corp., 99.8%) were further purified by heating under dynamic vacuum at 200° for 3 days, followed by treatment with a stream of freshly prepared dry hydrogen bromide for 2 hr while slowly raising the temperature to the melting point. Finally dry nitrogen was passed through the melt for 2 hr to remove all traces of the hydrogen bromide. The purified salts were stored in dark bottles in a drybox under an atmosphere of dry nitrogen, and all subsequent handling of the salts was done in the drybox. For cesium bromide it was found that filtering of the melt was required to remove particles of organic matter. Bromine (British Drug Houses Ltd., 99.0%) was redistilled in a fractionating column.

**Electrodes.** The silver electrode consisted of a 1-mm diameter silver lead (Johnson Matthey Chemicals Ltd., 99.999%) welded to a 10 cm long, 3.2-mm diameter silver rod (Halewood Chemicals Ltd., 99.999%). Bromine vapor passing over a spectroscopic grade graphite rod, of 3.2-mm diameter (Johnson Matthey Chemicals Ltd.), comprised the bromine electrode. Electrical contact with the graphite was provided by a tungsten wire through a Pyrex glass-to-metal seal. It has been found that an essential requirement for reversible and stable emf's involves the pretreatment of the graphite rods.<sup>4</sup> The rods were heated *in vacuo* for 72 hr at 500°, followed by heating in bromine in a closed tube at 500° for a further 72 hr.

**Cell.** A Vitreosil cell, similar to that described by Pelton and Flengas, was used.<sup>5</sup> The crucible containing the molten salts was positioned in the middle of a constant-temperature zone ( $\pm 0.5^\circ$  at 800° over 15 cm) in a nichrome-wound tube furnace. An important feature of the cell design was a high-impedance (about 20 kilohms) asbestos frit diaphragm which separated the two electrode compartments and prevented the diffusion of bromine to the silver electrode. Bromine was supplied at atmospheric pressure to the cell by a recirculating unit.<sup>6</sup>

**Measuring Apparatus.** Temperatures were measured with a Bureau of Standards calibrated chromel-alumel thermocouple, and cell emf's were amplified by a unity-voltage gain high-impedance (greater than  $10^{16}$  ohms) Keithley 640 electrometer, the voltage output being measured with a Pye (Model 7565) precision potentiometer, which was checked with a SE (Model SM 213 Mk.2) digital voltameter.

**Procedure.** The salts were weighed inside a drybox and placed in a quartz tube which was closed with a rubber stopper fitted with a vacuum stopcock. Once outside the drybox the tube was evacuated and the salts melted. After melting of the salts, the tube was rapidly cooled, returned to the drybox and broken open, and the salts were crushed to a fine powder using a Spex grinder. This ensured a homogeneous mixture which eliminated possible junction potentials across the frit diaphragm. The cell was loaded in the drybox, assembled under dry nitrogen in the furnace, and allowed to stand for 12 hr at a temperature just above the melting point of the mixture. Once bromine flow had commenced, 2-3 hr was required before stable ( $\pm 0.1$ mV) emf's were obtained. Approximately 1 hr was necessary after each temperature change for the emf to stabilize, the emf's being

(2) H. T. Davis and S. A. Rice, *J. Chem. Phys.*, **41**, 14 (1964).

(3) L. S. Hersh, A. Navrotsky, and O. J. Kleppa, *J. Chem. Phys.*, **42**, 3752 (1965).

(4) C. Dijkhuis, R. Dijkhuis, and G. J. Janz, *Chem. Rev.*, **68**, 253 (1968).

(5) A. D. Pelton and S. N. Flengas, *J. Electrochem. Soc.*, **117**, 1130 (1970).

(6) J. Leonardi and J. Brenet, *C. R. Acad. Sci., Ser. C*, **264**, 2090 (1967).

reproducible in both heating and cooling cycles. Cells were subjected to a polarization test in which 1 mA was passed through the cell in either direction using a 1.5-V dry cell. After the dry cell was disconnected, cell emfs returned to their original values within 1 min, thus confirming the reversibility of the cell.

### Results

**Silver-Carbon Thermocouple Correction.** The correction for the voltage due to the Ag-C thermocouple was determined by measuring the voltage of the cell with the silver wire connected to the graphite. Literature values<sup>7</sup> give the voltage as varying from 1.2 to 2.6 mV (silver positive with respect to the carbon) over the temperature range 500-900°, while Parish, *et al.*,<sup>8</sup> stated that the correction varied from 1 to 9 mV over the temperature range investigated. In Figure 1 are the results of Hamby<sup>9</sup> and those of Pelton and Flengas who stated that all previous values "appear questionable."

The voltage of the Ag-C couple was measured with several graphite rods produced by different Johnson Matthey Laboratories. Voltages were measured over the temperature range 200-900° and, for any particular silver-graphite rod couple, were found to be reproducible to 0.1 mV during successive heating and cooling cycles over several months. The correction values obtained for six different silver-graphite assemblies are shown in Figure 1, and it is apparent that the emf's obtained vary markedly from couple to couple. This effect may possibly be attributed to varying degrees of disorder in the layered structure of the graphite, affecting its electrical properties.

It is essential to obtain the relevant corrections for every Ag-C arrangement used, since the emf's were found to vary by as much as 12 mV from couple to couple even for graphite rods produced by the same laboratory.

**Formation Potential of Pure Silver Bromide.** The standard formation potentials,  $E^\circ$ , of the cell Ag(s)|AgBr(l)|Br<sub>2</sub>(g), C were determined in three separate experiments over the temperature range 440-870°. Using standard molar heat capacities at constant pressure<sup>6,10,11</sup> and the relationship  $\Delta C_p = nFT(\partial^2 E^\circ/\partial T^2)_p$ , it is found that the expected functional form of  $E^\circ$  is

$$E^\circ \text{ (mV)} = A + BT + 0.2319T \ln T - 4.55 \times 10^{-5} T^2 + 455.3/T \quad (1)$$

where  $T$  is in degrees Kelvin and  $A$  and  $B$  are integration constants. The measured emfs were corrected to 1 standard atm and further corrected for the voltage due to the Ag-C couple, and the 26 data points were fitted, using a linear least-squares method to an equation of the form of eq 1, giving

$$E^\circ \text{ (mV)} = 1153.9 - 1.9867T + 0.2319T \ln T - 4.55 \times 10^{-5} T^2 + 455.3/T \quad (2)$$

with the graphite positive with respect to the silver. In Table I the emf's at various temperatures calculated from eq 2 are compared with the results of previous work. The results of Metz and Seifert<sup>12</sup> were obtained using the electronic

(7) H. F. Stimson, J. F. Swindells, and R. E. Wilson, "American Institute of Physics Handbook," 2nd ed, McGraw-Hill, New York, N. Y., 1963, pp 4-7.

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

(9) D. C. Hamby, private communication quoted by Pelton and Flengas.<sup>5</sup>

(10) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, McGraw-Hill, New York, N. Y., 1961, p 66.

(11) G. J. Janz, "Molten Salts Handbook," Academic Press, New York, N. Y., 1967, p 200.

(12) C. R. Metz and R. L. Seifert, *J. Electrochem. Soc.*, **117**, 49 (1970).

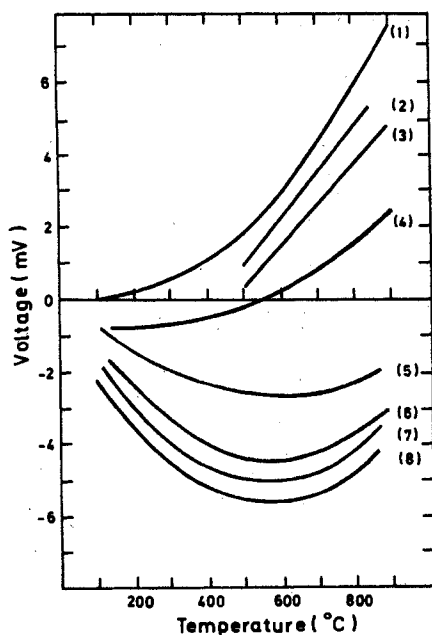


Figure 1. Ag-C thermocouple voltage vs. temperature (silver positive with respect to graphite): (1) Pelton and Flengas;<sup>5</sup> (2) Hamby;<sup>9</sup> (3)-(8) present results.

Table I. Standard Formation Potentials,  $E^\circ$  (mV), of Pure Silver Bromide at Various Temperatures

	500°	600°	700°	800°
Salstrom and Hildebrand <sup>14</sup>	786.4	757.6		
Murgulescu and Marchidan <sup>15</sup>	784.4	755.5		
Leonardi and Brenet <sup>6</sup>	779.8	753.8	727.3	701.0
Metz and Seifert <sup>12</sup>	780.6	754.0	729.5	706.8
Present study	783.7	756.3	730.7	706.6
Hamer, <i>et al.</i> <sup>13</sup>	781	754	706	

commutator method, claimed by the authors to give more accurate results than obtained from formation cells at high temperatures, while the results of Hamer, *et al.*,<sup>13</sup> were calculated from thermochemical data.

The standard formation potentials from the present study agree satisfactorily over a wide temperature range with those of Metz and Seifert<sup>12</sup> and those of Hamer, *et al.*<sup>13</sup> The results of Salstrom and Hildebrand<sup>14</sup> and of Murgulescu and Marchidan<sup>15</sup> cover only small temperature ranges due to the use of Pyrex apparatus, while Leonardi and Brenet<sup>6</sup> did not make any correction for the Ag-C thermocouple emf, which accounts for the low emf values at high temperatures.

**Binary Mixtures of AgBr and ABr (A = Li, Na, K, Rb, Cs).** Cell potentials,  $E$ , were measured during both heating and cooling cycles with melts at several different compositions in all the AgBr-ABr systems. In all cases the values of  $(E - E^\circ)$  as a function of temperature could be described by equations, obtained by a linear least-squares method, as shown in Table II. Typical plots of  $(E - E^\circ)$  vs. temperature for the AgBr-NaBr system are shown in Figure 2. The partial molar excess energies listed in Table II were fitted, using a linear least-squares method, to a power series of the form

$$\Delta F_{\text{AgBr}}^{\text{E}} = AX_{\text{ABr}}^2 + BX_{\text{ABr}}^3 + CX_{\text{ABr}}^4 + \dots \quad (3)$$

(13) W. J. Hamer, M. S. Malmberg, and B. Rubin, *J. Electrochem. Soc.*, 103, 8 (1956); 112, 750 (1965).

(14) E. J. Salstrom and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 52, 4650 (1930).

(15) I. G. Murgulescu and D. I. Marchidan, *Rev. Chim., Acad. Repub. Pop. Roum.*, 3, 47 (1958).

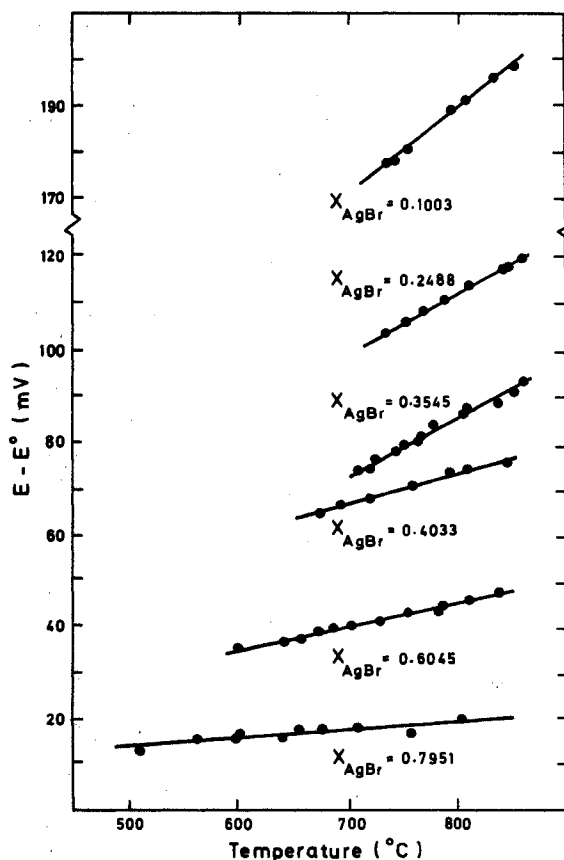


Figure 2. Values of  $E - E^\circ$  vs. temperature at various mole fractions for the AgBr-NaBr system.

where  $\Delta F_{\text{AgBr}}^{\text{E}}$  is the partial molar excess property in question,  $X_{\text{ABr}}$  is the mole fraction of alkali bromide and  $A$ ,  $B$ , and  $C$  are constants for each system and excess property. The fitted equations and mean and maximum deviations of the points for each fit are given in Table III.

**Excess Free Energies of Mixing.** Values of  $\Delta G_{\text{AgBr}}^{\text{E}}$  at 800° and of  $\Delta G_{\text{AgBr}}^{\text{E}}/X_{\text{ABr}}^2$ , for all systems, are plotted vs. composition in Figures 3 and 4. The fitted curves are obtained using eq 3 and the constants given in Table III. Straight lines are obtained from the plots of  $\Delta G_{\text{AgBr}}^{\text{E}}/X_{\text{ABr}}^2$  vs. composition in the AgBr-NaBr, AgBr-KBr, and AgBr-RbBr systems, indicating that two-coefficient power series are justified, while three-coefficient fits are justified in the AgBr-LiBr and AgBr-CsBr systems.

The present study is only the second in which it has been possible to define the second and third coefficients in the power expansion. Recently Pelton and Flengas<sup>5</sup> have determined these coefficients in the AgCl-Cl systems (A = Na, K, Rb, Cs). The regular solution theory of Hildebrand<sup>16</sup> predicts a power expansion of the form

$$\Delta G_{\text{AgBr}}^{\text{E}} = mX_{\text{ABr}}^2 \quad (4)$$

where  $m$  is an experimentally determined constant for the binary mixture investigated. Over their very limited temperature and composition ranges, Hildebrand and Salstrom found that their results fitted eq 4 very well. They did not investigate the AgBr-CsBr system. The present investigations show that at higher alkali bromide mole fractions deviations from eq 4 do occur, and these have to be compensated for by using further terms in the power expansion, showing that the

(16) J. H. Hildebrand, *J. Amer. Chem. Soc.*, 51, 66 (1929).

**Table II.** Linear Least-Squares Fits for  $(E - E^\circ)$  vs. Temperature at Various Compositions in the AgBr-ABr Systems (1 cal = 4.1840 J)

System	$X_{\text{AgBr}}$ , mole fraction	$E - E^\circ$ , mV ( $T$ , °K)	Mean dev, mV	Max dev, mV	$\overline{\Delta G_{\text{AgBr}}^E}(800^\circ)$ , cal mol <sup>-1</sup>	$\overline{\Delta H_{\text{AgBr}}}$ , cal mol <sup>-1</sup>	$\overline{\Delta S_{\text{AgBr}}^E}$ , cal mol <sup>-1</sup> deg <sup>-1</sup>
AgBr-LiBr	0.1156	-17.9 + 0.1223T	0.1	0.3	1984	412	-1.47
	0.1996	-21.0 + 0.0990T	0.3	0.7	1471	485	-0.92
	0.2888	-27.5 + 0.0892T	0.2	0.3	1079	635	-0.41
	0.3922	-29.4 + 0.0792T	0.6	0.7	715	679	-0.03
	0.5897	-19.9 + 0.0476T	0.6	1.1	403	459	0.05
AgBr-NaBr	0.7279	-13.5 + 0.0323T	0.5	0.8	190	311	0.11
	0.1003	-5.8 + 0.1786T	0.2	0.3	601	134	-0.44
	0.2488	-10.8 + 0.1146T	0.1	0.2	369	250	-0.11
	0.3545	-5.7 + 0.0847T	0.1	0.3	239	132	-0.10
	0.4033	-5.1 + 0.0736T	0.2	0.4	224	117	-0.10
AgBr-KBr	0.6045	-2.9 + 0.0441T	0.1	0.2	46	67	0.02
	0.7951	4.9 + 0.0150T	0.3	0.7	4	-113	-0.11
	0.0693	101.5 + 0.1843T	0.1	0.3	-1211	-2342	-1.05
	0.0988	90.1 + 0.1622T	0.3	0.5	-1156	-2077	-0.86
	0.2342	60.1 + 0.1051T	0.2	0.4	-960	-1455	-0.46
AgBr-RbBr	0.3904	38.3 + 0.0661T	0.3	0.7	-512	-882	-0.35
	0.6097	14.1 + 0.0416T	0.4	0.9	-299	-325	-0.02
	0.0622	139.5 + 0.1876T	0.3	0.7	-1936	-3216	-1.19
	0.1461	119.3 + 0.1230T	0.3	0.6	-1694	-2752	-0.99
	0.2640	86.1 + 0.0886T	0.2	0.3	-1339	-1985	-0.60
AgBr-CsBr	0.4695	44.6 + 0.0536T	0.4	0.5	-742	-1028	-0.27
	0.6397	22.9 + 0.0311T	0.4	0.9	-346	-528	-0.17
	0.7813	10.9 + 0.0178T	0.3	0.6	-165	-250	-0.08
	0.0488	191.8 + 0.2148T	0.3	0.5	-3117	-4423	-1.22
	0.1051	178.5 + 0.1481T	0.1	0.1	-2995	-4117	-1.05
	0.1997	150.0 + 0.1069T	0.2	0.3	-2673	-3461	-0.77
	0.3791	107.4 + 0.0606T	0.1	0.4	-1908	-2478	-0.53
	0.6202	45.8 + 0.0350T	0.2	0.6	-901	-1056	-0.15
	0.8512	2.9 + 0.0186T	0.2	0.4	-183	-67	0.11

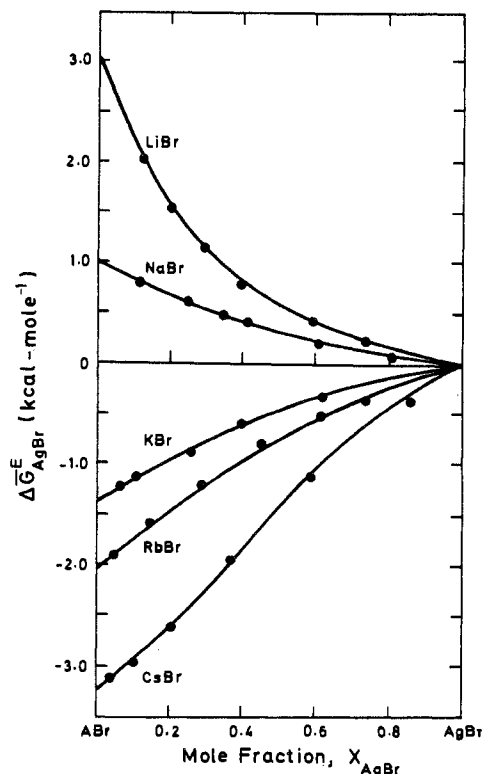
**Table III.** Least-Squares Fits for the Partial Molar Excess Properties of Mixing of AgBr vs. Composition in the AgBr-ABr Systems

System	A	B	C	Mean dev	Max dev
$\overline{\Delta G_{\text{AgBr}}^E}(800^\circ)$ , cal mol <sup>-1</sup>					
AgBr-LiBr	4316	-7668	6406	16	32
AgBr-NaBr	188	617		11	25
AgBr-KBr	-1753	353		40	60
AgBr-RbBr	-3266	1120		16	26
AgBr-CsBr	-8029	4951	-146	16	23
$\overline{\Delta H_{\text{AgBr}}}$ , cal mol <sup>-1</sup>					
AgBr-LiBr	4670	-4757		32	67
AgBr-NaBr	670	-506		49	130
AgBr-KBr	-1744	-974		24	52
AgBr-RbBr	-3911	247		40	65
AgBr-CsBr	-8942	4287		45	116
$\overline{\Delta S_{\text{AgBr}}^E}$ , cal mol <sup>-1</sup> deg <sup>-1</sup>					
AgBr-LiBr	3.214	-5.746		0.04	0.09
AgBr-NaBr	0.451	-1.051		0.05	0.11
AgBr-KBr	0.203	-1.455		0.06	0.10
AgBr-RbBr	-0.599	-0.815		0.04	0.05
AgBr-CsBr	-0.928	-0.409		0.05	0.13

solutions are not regular. Values for the integral molar excess Gibbs free energy of mixing may be obtained by numerical integration using the Gibbs-Duhem relation. These values may be fitted to an equation of the form

$$\Delta G^E = X(1-X)(a + bX + cX(1-X)) \quad (5)$$

where  $X$  is the silver bromide mole fraction. The values of the constants  $a$ ,  $b$ , and  $c$  may be obtained from a direct plot of  $\Delta G^E/X(1-X)$  vs.  $X$  using values of  $\Delta G^E$  obtained from the Gibbs-Duhem relation or analytically from the constants  $A$ ,  $B$ , and  $C$  from eq 3. Both methods give identical values for  $a$ ,  $b$ , and  $c$  which are listed in Table IV. Estimates of the errors in the parameters  $a$ ,  $b$ , and  $c$  may be obtained from the elements of the covariance matrix, as described by Went-

**Figure 3.** Values of the partial molar excess free energy of mixing,  $\Delta G_{\text{AgBr}}^E$ , vs. mole fraction for the AgBr-ABr systems.

worth.<sup>17</sup> At 0.5 mole fraction the standard deviations in  $\Delta G^E$  are 60, 15, 47, 15, and 43 cal mol<sup>-1</sup> for the LiBr to CsBr systems, respectively.

**Enthalpies of Mixing.** Values for the integral molar en-

(17) W. E. Wentworth, *J. Chem. Educ.*, 42, 96 (1965).

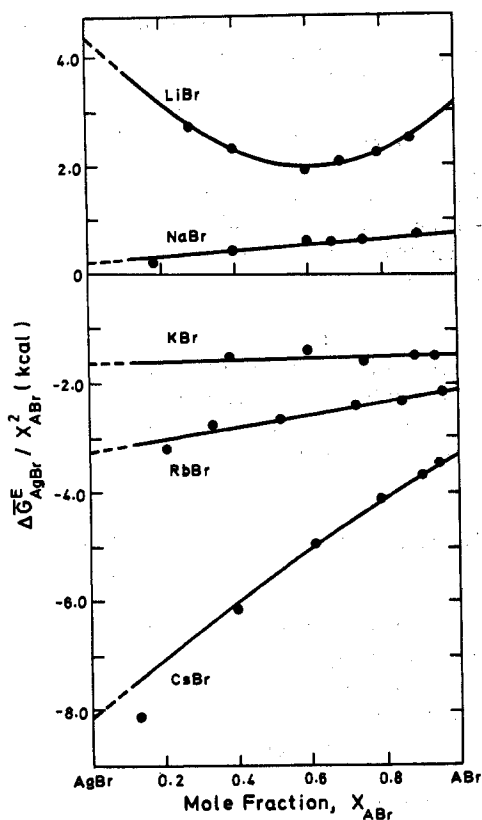


Figure 4. Values of  $\Delta \overline{G}_{\text{AgBr}}^E / X_{\text{AgBr}}^2$  vs. mole fraction for the AgBr-ABr systems.

Table IV. Least-Squares Fits for the Integral Molar Excess Energies of Mixing vs. Composition in the AgBr-ABr Systems

System	a	b	c
	$\Delta G^E(800^\circ), \text{cal mol}^{-1}$		
AgBr-LiBr	3054	-436	2135
AgBr-NaBr	808	-310	
AgBr-KBr	-1400	-176	
AgBr-RbBr	-2145	-560	
AgBr-CsBr	-3224	-2378	50
	$\Delta H^M, \text{cal mol}^{-1}$		
AgBr-LiBr	-87	2379	
AgBr-NaBr	164	253	
AgBr-KBr	-2717	487	
AgBr-RbBr	-3664	-124	
AgBr-CsBr	-4654	-2144	
	$\Delta S^E, \text{cal mol}^{-1} \text{ deg}^{-1}$		
AgBr-LiBr	-2.532	2.873	
AgBr-NaBr	-0.601	0.526	
AgBr-KBr	-1.252	0.728	
AgBr-RbBr	-1.415	0.408	
AgBr-CsBr	-1.336	0.204	

thality of mixing,  $\Delta H^M$ , obtained by numerical integration using the Gibbs-Duhem relation, are plotted vs. composition (Figure 5) for comparison with the values of Hersh, *et al.*,<sup>3</sup> obtained by calorimetric means.

Good agreement is found for all systems except the AgBr-NaBr systems. The maximum operating temperature of the calorimeter used by Hersh, *et al.*, was approximately 700°. This temperature is below the melting points of sodium and potassium bromide, so that in order to obtain the liquid-liquid enthalpy of mixing,  $\Delta H_{1-1}$ , the solid-liquid enthalpy of mixing,  $\Delta H_{s-1}$ , must be corrected for the heat of fusion,  $\Delta H_f$ , of the alkali bromide

$$\Delta H_{1-1} = \Delta H_{s-1} - X_{\text{ABr}} \Delta H_f \quad (6)$$

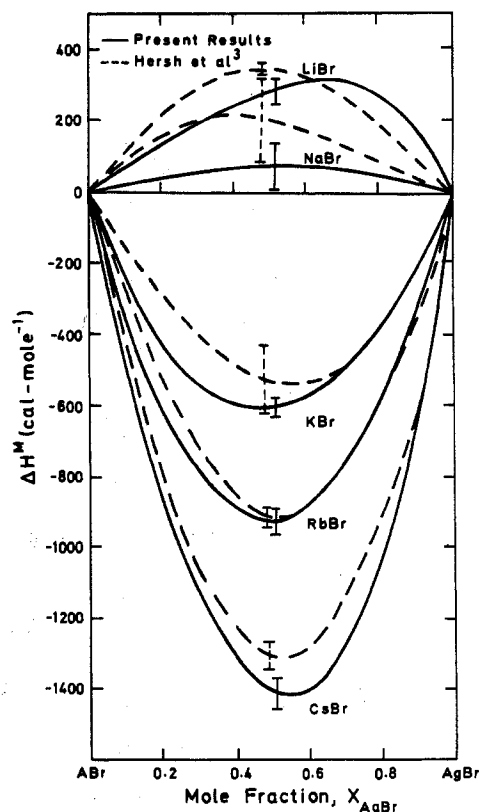


Figure 5. Values of the heat of mixing,  $\Delta H^M$ , vs. mole fraction for the AgBr-ABr systems, compared with the results of Hersh, *et al.*<sup>3</sup>

Hersh, *et al.*, adopted the measured heats of fusion of Dworkin and Bredig<sup>18</sup> and the values of  $\Delta C_p$  for the process of fusion given by Kleppa and Meschel.<sup>19</sup> These values have a quoted uncertainty<sup>18</sup> of 2%, and hence it may easily be shown that the heat of fusion of sodium bromide at 705° (the temperature of the calorimeter used by Hersh, *et al.*) is  $6.157 \pm 0.123 \text{ kcal mol}^{-1}$ . Hersh, *et al.*, stated that the uncertainty involved in the determination of  $\Delta H_{s-1}$  is also 2%. The value of  $\Delta H_{s-1}$  for silver bromide (liquid) and sodium bromide (solid) measured by Hersh, *et al.*,<sup>3</sup> at, for example,  $X_{\text{AgBr}} = 0.4972$  is  $3.308 \text{ kcal mol}^{-1}$ . Thus  $\Delta H_{1-1}$  is given by

$$\Delta H_{1-1} = 3.308 \pm 0.066 - 0.5028(6.157 \pm 0.123) \text{ kcal mol}^{-1} = 212 \pm 128 \text{ cal mol}^{-1}$$

The corresponding uncertainty at 0.5 mol fraction for the AgBr-KBr system is  $110 \text{ cal mol}^{-1}$ . The standard deviations<sup>17</sup> of our measured  $\Delta H$  values and those calculated<sup>17</sup> from the data of Hersh, *et al.*,<sup>3</sup> are represented by error bars in Figure 5, and it is seen that the agreement between our enthalpies and those of Hersh, *et al.*,<sup>3</sup> is satisfactory, the AgBr-NaBr discrepancy having been accounted for.

The values of  $\Delta H^M$  may be fitted to an equation similar to eq 5 and the constants are listed in Table IV.

**Excess Entropies of Mixing.** In Figure 6 the integral molar excess entropies of mixing are plotted vs. composition. Values of  $\Delta S^E$  may be fitted to an equation similar to eq 5, and the constants are listed in Table IV. Together with the excess entropies of Pelton and Flengas<sup>5</sup> for the AgCl-ACl systems, these are the only precise excess entropies of mixing for molten salt mixtures yet published.

(18) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 269 (1960).

(19) O. J. Kleppa and S. V. Meschel, *J. Phys. Chem.*, **67**, 668 (1963).

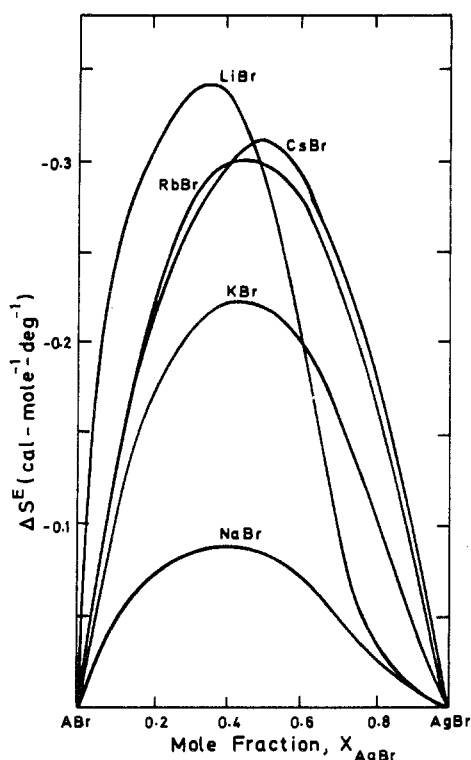
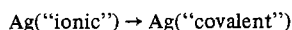


Figure 6. Values of the excess entropy of mixing,  $\Delta S^E$ , vs. mole fraction for the AgBr-ABr systems.

### Discussion

A simple structural model for interpreting thermodynamic energies of mixing for the silver halide-alkali halide molten systems has recently been developed by Pelton and Flengas.<sup>5</sup> Their model has been applied to the silver chloride-alkali chloride mixtures, as well as the magnesium chloride-alkali chloride<sup>20</sup> and manganous chloride-alkali chloride systems.<sup>21</sup>

In the AgCl-ACl systems it was proposed that a fraction ( $\alpha$ ) of the silver exists as 100% "ionically" bonded silver (electrostatic interactions only), and the remainder ( $1 - \alpha$ ) of the silver interacts covalently with surrounding ions. It was further assumed that the two types of silver can exchange positions with each other and with alkali cations on cation sites. On the basis of a simple statistical model an equation in  $\alpha$  and  $\alpha^0$  was obtained for the excess entropy of mixing, where  $\alpha = \alpha^0$  in pure silver halide. Assigning  $\Delta e_1$  to the molar energy change for the process



occurring in pure silver bromide, and  $\Delta e_2$  to the molar energy change for the same process occurring at infinite dilution in alkali halide solvent, it was shown that the enthalpy of mixing was given by

$$\Delta H^M = X_{\text{Ag}}(\alpha - \alpha^0)\Delta e_1 + \alpha X_{\text{Ag}}X_{\text{A}}b \quad (7)$$

where  $b = \Delta e_2 - \Delta e_1$ . It was shown that  $\alpha$  and  $\alpha^0$  could be represented in terms of  $\Delta e$  and  $b$ :  $\alpha^0 = c_1/(1 + c_1)$  where  $c_1 = \exp(-\Delta e_1/RT)$ ;  $\alpha = c_1c_2/(1 + c_1c_2)$  where  $c_2 = \exp(-X_{\text{A}}b/RT)$ . If values of  $\Delta e_1$  and  $b$  are chosen, the above set of equations may be used to give numerical solutions of  $\Delta H^M$  and  $\Delta S^E$  at any composition. For any particular silver halide-alkali halide system, parameter  $\Delta e_1$  is independent of

(20) A. D. Pelton and W. T. Thompson, *Can. J. Chem.*, **48**, 1585 (1970).

(21) A. S. Kucharski and S. N. Flengas, *J. Electrochem. Soc.*, **119**, 1170 (1972).

the alkali cation, while  $b$  has a different value for each binary mixture. Pelton and Flengas<sup>5</sup> found that good fits to their experimental results for the AgCl-ACl systems ( $A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) were obtained with  $\Delta e_1 = -3.5$  kcal and  $b$  values of 1.5, -2.0, -3.0, and -4.5 kcal for Na to Cs, respectively, giving an  $\alpha^0$  value corresponding to 83.6% of the silver cations having a degree of covalent bonding. Clearly,  $\alpha^0$  should increase for the silver bromide-alkali bromide systems. The Pelton-Flengas theory was applied to our results for the silver bromide-alkali bromide systems in order to test this prediction.

Good fits ( $\pm 3\%$ ) to the experimental enthalpies of mixing were obtained for all systems with  $\Delta e_1 = -4.2$  kcal (with  $\alpha^0 = 0.878$ ) and  $b$  values of 1.0, 0.3, -2.2, -3.4, and -5.2 kcal for the AgBr-LiBr, -NaBr, -KBr, -RbBr, and -CsBr systems, respectively. However, the excess entropy of mixing fits were poor to the extent that the theory did not even predict the correct sign of  $\Delta S^E$  for the LiBr and NaBr systems. With  $\Delta e_1 = 0.06$  kcal and  $b = 4.4, 0.6, -3.6, -5.0,$  and  $-7.0$  kcal for Na to Cs the entropy fits were improved and signs corrected. However now  $\alpha^0 = 0.493$  and enthalpy fits become much poorer ( $\pm 9\%$ ). It thus appears that the Pelton-Flengas theory is able to reproduce the experimental enthalpies and excess entropies of mixing, but the facts that six adjustable parameters are used and that these parameters may vary by orders of magnitude and still obtain acceptable values for  $\Delta H^M$  and  $\Delta S^E$  make any physical significance attached to the parameters seem unjustified.

The only rigorous theory as yet for the energies of mixing is that of Reiss, Katz, and Kleppa<sup>22</sup> (RKK), which is essentially an adaptation of the theory of conformal solutions, in which no model is used. The theory was further developed by Davis and Rice<sup>2</sup> (DR), who included dispersion interactions to give the pair potential between ions. The result obtained is

$$\Delta A^{E_{12}} = X_1X_2(U_0 + U_1\delta_{12} + U_2\delta_{12}^2) \quad (8)$$

where  $U_0$  is attributed to van der Waals-London dispersion forces between next nearest neighbor cations;  $U_1$  depends primarily on the difference between cation-anion dispersion interactions in each of the two components of the mixture and may also account for changes in energy due to covalent bonding;  $X$  is mole fraction,  $\Delta A^E$  is excess Helmholtz free energy, and  $\delta_{12} = (d_2 - d_1)/d_1d_2$  where  $d_i$  is the radius of the  $i$ th cation. Although  $U_2$  represents coulombic energies, it also contains a term which depends on the sum of cation-anion dispersion interaction in the two components of the mixture.

The DR theory predicts values for the excess Helmholtz free energy of mixing. We have

$$\Delta A^E = \Delta H^M - T\Delta S^E + P\Delta V^M \quad (9)$$

Since all experimental measurements are conducted at nearly atmospheric pressure,  $P\Delta V^M$  is small. Furthermore, Hersh and Kleppa<sup>23</sup> quoted results of Hildebrand and Salstrom<sup>24</sup> which suggested that many uni-univalent molten salt mixtures form essentially regular solutions, resulting in a small  $\Delta S^E$ . Consequently, the convenient but unnecessary assumption<sup>25</sup> was made that

(22) H. Reiss, J. L. Katz, and O. J. Kleppa, *J. Chem. Phys.*, **36**, 144 (1962).

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

(24) J. H. Hildebrand and E. J. Salstrom, *J. Amer. Chem. Soc.*, **54**, 4257 (1932).

(25) K. D. Luks and H. T. Davis, *Ind. Eng. Chem., Fundam.*, **6**, 194 (1967).

$$\Delta H^M = \Delta A^E \quad (10)$$

Hersh and Kleppa measured the heats of mixing of the binary alkali halides and binary alkali nitrates and found them to be well fitted by the equation

$$\Delta H^M = X_1 X_2 (U_0 - 340\delta_{12}^2) \quad (11)$$

with London forces calculated by a method similar to that of Meyer<sup>26</sup> for the solid alkali halides.

Hersh, *et al.*,<sup>3</sup> fitted the DR theory to their measured heats of mixing of the silver bromide-alkali bromide systems. Deviations from eq 11 were found so that it was necessary to include the term  $U_1\delta_{12}$ . Representing  $U_0 - 340\delta_{12}^2$  by  $\lambda$ , the value of  $U_1$  was found by plotting  $4\Delta H^M_{0.5} - \lambda$  vs.  $\delta_{12}$ , arriving at  $U_1 = 52$  kcal Å. However, the theoretical  $\Delta H^M$  predicted for the AgBr-LiBr system was in error by about 1200 cal. Our measurements show that this discrepancy is due to the neglect of the term  $-T\Delta S^E_{0.5}$  and that  $\Delta S^E$  is not negligible.

It has been found<sup>24</sup> that  $P\Delta V_{0.5}$  does not exceed 0.02 cal mol<sup>-1</sup> for the silver bromide-alkali bromide systems; confirming that  $\Delta A^E = \Delta G^E$ . Since no previous test of the Davis-Rice theory has used  $\Delta G^E$ , there is no previously obtained value for  $U_2$ . The best fit to our results was obtained with  $U_2 = -288$  kcal Å<sup>2</sup> mol<sup>-1</sup>. Representing  $U_0 - 288\delta_{12}^2$  by  $\lambda'$ , our values for  $4\Delta G^E_{0.5} - \lambda'$  at 800° and  $4\Delta H^M_{0.5} - \lambda$  of Hersh, *et al.*,<sup>3</sup> are plotted vs.  $\delta_{12}$  in Figure 7. Pauling radii have been used except for the silver cation radius, where the value of 0.95 Å suggested by Blander<sup>27</sup> has been used. The values of  $U_0$  were calculated by the method of Meyer,<sup>26</sup> which was also the procedure used by Hersh, *et al.*<sup>3</sup>

The slope for the excess free energies is 40 kcal Å mol<sup>-1</sup>, so that

$$\Delta G^E = X_1 X_2 (U_0 + 40\delta_{12} - 288\delta_{12}^2) \text{ kcal mol}^{-1} \quad (12)$$

The fit using the excess free energies of mixing is very good, whereas the fit assuming  $\Delta A^E = \Delta H^M$  is poor for silver bromide-lithium bromide mixtures as shown in Figure 7 which illustrates that the assumption in eq 10 is invalid. The value of  $\Delta S^E_{0.5}$  for the silver bromide-lithium bromide system is 0.27 cal mol<sup>-1</sup> deg<sup>-1</sup>, so that at 800° the value of  $4T\Delta S^E_{0.5}$  is 1160 cal mol<sup>-1</sup>, accounting for the error obtained by Hersh, *et al.*,<sup>3</sup> when using the approximation in eq 10.

Excess free energies of mixing calculated from eq 12 are compared with the experimental values in Figure 8, which shows that the Davis-Rice theory is able to predict excess free energies of mixing for molten salt mixtures. No previous  $\Delta G^E$  values involving mixing with the Li<sup>+</sup> ion are available to test theoretical predictions of  $\Delta G^E$  such as in eq 12.

From the functional form of the terms  $U_0$ ,  $U_1$ , and  $U_2$  appearing in the DR theory,<sup>2</sup> it may be seen that  $U_0$  is independent of temperature and pressure, while  $U_1$  and  $U_2$  are functions of temperature and pressure. Therefore since  $\Delta S^E = -(\partial G^E/\partial T)_P$ , we may write

$$\Delta S^E = -X_1 X_2 (U_1' \delta_{12} + U_2' \delta_{12}^2) \quad (13)$$

There is no way directly to calculate  $U_1'$  ( $=\partial U_1/\partial T$ ) and  $U_2'$  ( $=\partial U_2/\partial T$ ) from the values of  $U_1$  and  $U_2$ , but a linear least-squares fit of eq 13 to our experimentally measured  $\Delta S^E$  gives

$$\Delta S^E = -X_1 X_2 (2.77\delta_{12} + 370\delta_{12}^2) \text{ cal mol}^{-1} \text{ deg}^{-1} \quad (14)$$

In Table V the experimentally measured excess entropies are compared with those calculated using eq 14. The agreement is very satisfactory.

As the only previous precise entropy of mixing data available<sup>5</sup> did not include measurements on the silver chloride-lithium chloride system, no other significant test of this extension of the DR theory to include prediction of excess entropies of mixing is possible. However, our results appear

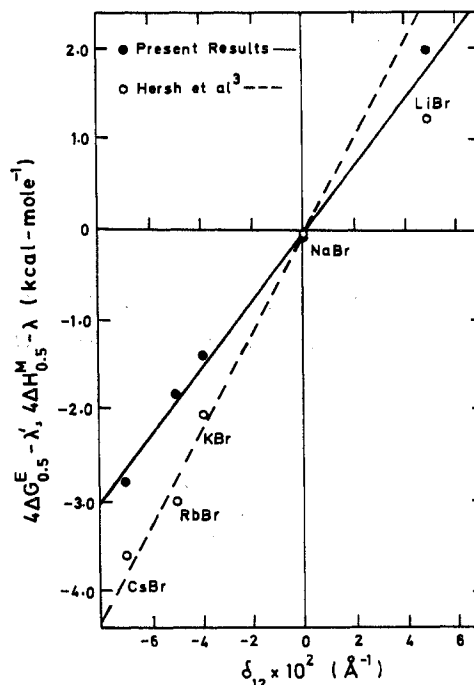


Figure 7. Values of  $4\Delta G^E_{0.5} - \lambda'$  vs.  $\delta_{12}$  for the AgBr-ABr systems, compared with the values  $4\Delta H^M_{0.5} - \lambda$  measured by Hersh, *et al.*<sup>3</sup>

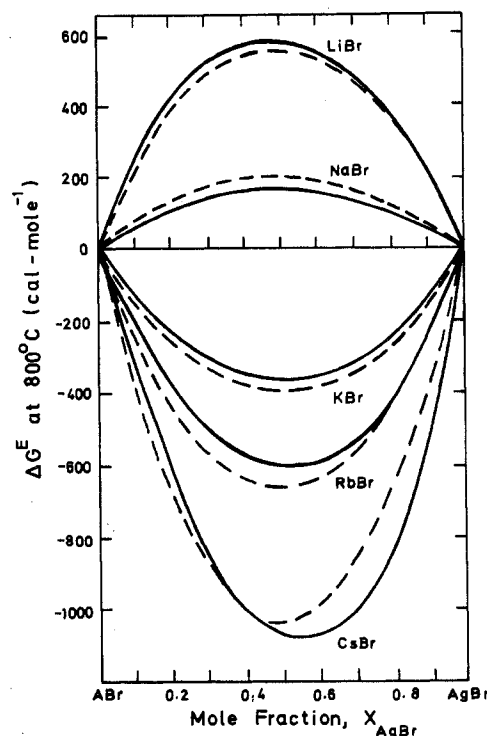


Figure 8. Experimental values of  $\Delta G^E$  vs. mole fraction for the AgBr-ABr systems, compared with values of  $\Delta G^E$  calculated using the Davis-Rice theory: —, measured; ----, calculated.

(26) S. Meyer, *J. Chem. Phys.*, 1, 270 (1933).

(27) M. Blander, *J. Chem. Phys.*, 36, 1092 (1962).

**Table V.** Values of the Experimentally Obtained Excess Entropies of Mixing  $\Delta S^E_{\text{exptl}}$  and the Calculated Entropies  $\Delta S^E_{\text{calcd}}$  at 0.5 Mole Fraction

System	$\delta_{12}, \text{\AA}^{-1}$	$\Delta S^E_{\text{exptl}},$ cal mol <sup>-1</sup> deg <sup>-1</sup>	$\Delta S^E_{\text{calcd}},$ cal mol <sup>-1</sup> deg <sup>-1</sup>
AgBr-LiBr	0.0473	-0.27	-0.24
AgBr-NaBr	0.0000	-0.08	0.00
AgBr-KBr	-0.0399	-0.22	-0.12
AgBr-RbBr	-0.0533	-0.30	-0.23
AgBr-CsBr	-0.0701	-0.31	-0.40

to indicate the correctness of the functional form<sup>2</sup> of eq 8 predicted from conformal solution theory, and the  $\Delta G^E =$

$\Delta H^M$  assumption made in previous published work is shown to be invalid.

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**Registry No.** LiBr, 7550-35-8; NaBr, 7647-15-6; KBr, 7758-02-3; RbBr, 7789-39-1; CsBr, 7787-69-1; AgBr, 7785-23-1.

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## Adducts of Chlorine Oxide Trifluoride with Group V Element Pentafluorides. Structural Study of the Hexafluoro Anions

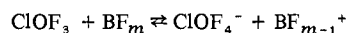
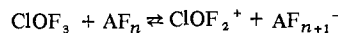
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Received April 23, 1973

The adduct formation of ClOF<sub>3</sub> with PF<sub>5</sub>, AsF<sub>5</sub>, VF<sub>5</sub>, SbF<sub>5</sub>, TaF<sub>5</sub>, NbF<sub>5</sub>, and BiF<sub>5</sub> was studied. With each of these pentafluorides a one-to-one complex is formed and characterized by X-ray powder diffraction patterns and vibrational spectra. The latter strongly support ionic structures. Both orbital valence and Urey-Bradley force fields were computed and evaluated for PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, VF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, TaF<sub>6</sub><sup>-</sup>, NbF<sub>6</sub><sup>-</sup>, and BiF<sub>6</sub><sup>-</sup>.

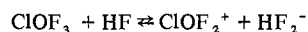
### Introduction

Chlorine oxide trifluoride exhibits amphoteric properties. It forms adducts with Lewis bases or acids<sup>1-6</sup> according to



where AF<sub>n</sub> and BF<sub>m</sub> stand for acid and basic molecules, respectively.

We have previously shown<sup>1</sup> that ClOF<sub>3</sub> is ionized in anhydrous HF according to



Likewise Christe, *et al.*,<sup>2-4</sup> described examples of adducts derived from both acids and bases. In this paper we wish to report the basic property of ClOF<sub>3</sub> toward group V element pentafluorides.

Adducts of ClOF<sub>3</sub> with AsF<sub>5</sub> and SbF<sub>5</sub> have already been reported elsewhere.<sup>1,2,4,5</sup> In this paper we report the results of a systematic study involving a large number of pentafluorides.

### Experimental Section

**Materials.** Chlorine oxide trifluoride has been prepared either according to a photolytic process<sup>1</sup> or, with a much better yield, according to the chemical process described by Pilipovich, *et al.*<sup>7</sup> ClOF<sub>3</sub> was stored as a complex with KF to prevent any decomposi-

(1) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **273**, 415 (1971).

(2) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 2205 (1972).

(3) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2209 (1972).

(4) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, **11**, 2212 (1972).

(5) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **271**, 1366 (1970).

(6) K. Zuchner and O. Glemser, *Angew. Chem.*, **84**, 1147 (1972).

(7) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

tion during storage. Impurities not forming a stable KF adduct are pumped off at 25° while pure ClOF<sub>3</sub> is obtained by vacuum pyrolysis at 60-80°.

SbF<sub>5</sub> was purchased from the Societe des Usines Chimiques de Pierrelatte and the other pentafluorides were prepared<sup>8</sup> by reaction between fluorine and the corresponding elements (purchased from Prolabo). Prior to use, the volatile pentafluorides were purified by fractional condensation and checked for purity by Raman and infrared spectroscopy, powder X-ray diffraction pattern, and microsublimation whenever the physical state of the sample allowed these methods to be used.

**Apparatus.** The "fluorine line" used in this work is for the most part made of Monel metal tubing equipped with valves purchased from F.W. Co. and Etudes et Constructions Aeronautiques Co. (ECA) differential gauges for the ranges 0-10 and 0-100 mm and with Bourdon gauges for the ranges 0-100 and 0-5000 mm. Occasionally we have also used an Atlas MCT manometer for the very low pressure measurements. For observation, part of the apparatus was equipped with Kel-F tubes and Kel-F valves purchased from Viennot Co.

Before use the vacuum line was passivated with ClF<sub>3</sub> and the compound to be handled. We noticed this procedure to be specially useful whenever ClOF<sub>3</sub> is handled; otherwise slight amounts of ClO<sub>2</sub>F were produced.

**Spectra.** Infrared spectra were recorded with a Beckman Model IR 9 and a Perkin-Elmer Model 457 in the ranges 4000-400 and 4000-250 cm<sup>-1</sup>, respectively, while an FS 720 spectrophotometer was used in the 400-40-cm<sup>-1</sup> range.

Spectra of gases were recorded using a 10 cm long Monel-body gas cell equipped with AgCl windows sealed with Teflon gaskets. Powders were pressed between two thin plates of AgCl 12 mm in diameter. In order to prevent loss of energy due to the IR 9 beam height which is larger than the pellet diameter we used a beam condenser with this apparatus.

Rather good spectra in the lower frequency range could be obtained by using two silicon plates (29 mm in diameter and 1 mm in thickness, Silicon Z F chemical polish type, 30-50 ohm/cm, purchased from Silec Co). The powders were put between these plates probably due to their highly polished surface, the attack was slow

(8) A. D. Beveridge and H. C. Clark, *Halogen Chem.*, **3**, 91 (1967); F. Fairbrother, *ibid.*, **3**, 123 (1967); L. Kolditz, *ibid.*, **2**, 116 (1967).