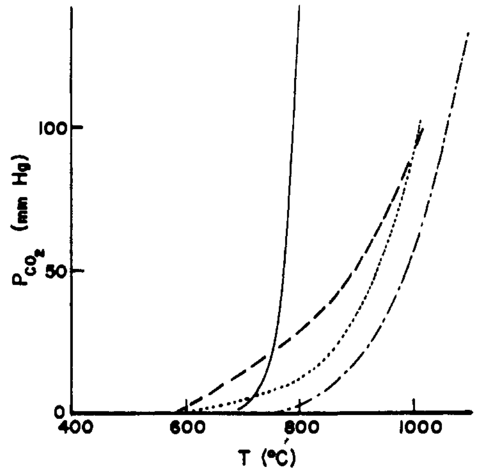

Figure 1. Comparison of equilibrium dissociation pressures for Li_2CO_3 gained by the dynamic method and from static technique
Static techniques: data of Lebeau (5), — — — —; Johnston (4) ......; and Howarth and Turner (3), — · — · — · — · Dynamic technique; present investigation ————————.

where cognizance of the activities of the oxide and the carbonate in the liquid mixture as well as the CO_2 pressure in the reaction equilibrium is important. The significance of this point seems to have escaped the earlier experimentalists (*3, 4, 5*). The vacuum drying techniques at elevated temperatures for removal of water vapor, common practice in the preparation of dry samples for static measurements, introduce a factor of uncertainty by simultaneous removal of CO_2 and consequent formation of M_2O in the sample. The displacement of the curves in Figure 1 is understood in large part from this viewpoint. At 775° C. for example, the results of Lebeau (*5*), Johnston (*4*), and Howarth and Turner (*3*) can be brought into accord with the present data if a correction for 0.004, 0.02, and 0.1 mole Li_2O/per mole Li_2CO_3 is made for the equilibria in the molten specimens.

Both Li_2CO_3 and Na_2CO_3 show first appreciable dissociation just above their respective melting points. This may be attributed in part to the smaller interatomic distances in the molten salts compared with the solid state (*6*).

Effectively, this predicts a sudden increase in the polarizing effect of the cationic species at the melting point of the inorganic salt with the transition of the salt through fusion from the solid state to the liquid state. For both Li_2CO_3 and Na_2CO_3, the first appreciable dissociation pressures are observed on fusion. This factor, and the significantly greater dissociation pressures of Li_2CO_3 relative to Na_2CO_3 correlate with the polarizing power of the cationic species.

The following points should be noted relative to the dynamic and static methods in such studies. When measuring dissociation pressures by the dynamic method, the effects of any residual water and impurities present in the sample are of little importance. The rate of dissociation may be affected but not the equilibrium. In the case of the static pressure method, any impurity leading to a stable gas phase will contribute an error to the measured dissociation pressure. By contrast, a finite vapor pressure of the salt would contribute to an error in the dynamic, but not in the static method.

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Fused Salt Distribution Studies

Distribution of TlBr Between KNO_3 and AgBr

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IN A PREVIOUS PUBLICATION (*3*), the distribution constant for TlCl between KNO_3 and AgCl:

$$K = [TlCl]_{KNO_3}/[TlCl]_{AgCl}$$

and the association constant, *k*, for:

$$Tl^+ + Cl^- \xrightarrow{k} TlCl$$

in molten KNO_3 were obtained from the following equation:

$$K_o = K + (K/k)[X^-]^{-1} \qquad (1)$$

K_o was the observed distribution coefficient, K the distribution constant for TlCl, k the association constant, and $[X^{-1}]$ was the halide ion concentration in the KNO_3 phase.

The same relationship was displayed by the TlBr distribution between KNO_3 and AgBr, and in this study the temperature dependence of K and k was investigated.

EXPERIMENTAL

The same apparatus used for TlCl distribution (*3*) was used for the TlBr distributions. However, a Vycor flask was used in place of the borosilicate glass flask for distributions at temperatures above 500° C. Normally, 50 grams

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The distribution coefficient for TlBr between KNO_3 and AgBr was measured at temperatures between 450° and 550° C. in a series of experiments in which KBr was added to vary the bromide ion concentration in the KNO_3 phase. The association constant in KNO_3 and distribution constant for TlBr were determined from the results by the method of least squares. The distribution constant, $[TlBr]_{KNO_3}/[TlBr]_{AgBr}$, was approximately 0.07 in this temperature range and increased slightly with increasing temperature. The association constant decreased from 2.6 (moles/kg.)$^{-1}$ at 450° C. to 1.9 at 550° C.

of KNO_3 and 50 grams of AgBr were melted under controlled temperature conditions with a Wheelco electronic temperature controller ($\pm 3°$ C.). A quantity of potassium bromide and 500 mg. of TlBr were added, and the mixture was stirred for 10 minutes. The two phases were allowed to separate. The plug of frozen salt in the capillary outlet was melted by turning on the auxiliary heater, and the molten mixture flowed into the sample collector. Several portions of each phase were collected and analyzed.

Thallium was determined polarographically in 1*F* citric acid (pH 3.0) as supporting electrolyte. The AgBr phases were dissolved in KCN. After addition of citric acid, the AgBr was precipitated by further acidification which left the thallium in solution.

The solubility of AgBr in molten KNO_3 was found by drawing samples from the top of the two-phase system (to avoid collecting droplets of the silver bromide phase when the mixture flowed out the capillary outlet), and weighing the amount of silver bromide which remained undissolved when the sample was treated with water. The solubilities are given in Table I.

The bromide ion concentration in the KNO_3 phase was determined by one of two methods. Total bromide was determined by dissolving the sample in water, adding 1*F* $AgNO_3$ until precipitation ceased, filtering, drying, and weighing. Since this method included bromide which had been complexed as AgBr and $AgBr_2^-$ in the fused KNO_3, the complex constants had to be determined in order to calculate bromide ion concentrations. The constants (K_{sp}, K_1 and K_2 for AgBr in molten KNO_3) were estimated for these experimental conditions from published constants and the solubility of AgBr in KNO_3 (Table I). The following equation (*4*), previously developed, was used:

$$[Br^-] = \frac{\text{total} - K_1K_{sp}}{1 + 2K_1K_2K_{sp}}$$

This method for finding total bromide gave poor reproducibility at low bromide concentration, and the error was attributed to some samples containing droplets of AgBr physically entrapped when the solvents flowed out the capillary outlet.

A new method was developed which avoided this possible error. In this method, the AgBr present when the potassium nitrate sample was dissolved in water was filtered off before precipitation of bromide as AgBr. The subsequent precipitate of AgBr represented the total bromide minus an amount of bromide equivalent to the silver present. Since the preliminary precipitation included any AgBr which had been physically entrapped, the source of error was eliminated. Duplicate determinations checked within 0.5%.

Table I. Solubility of AgBr in KNO_3

Temp., ° C.	Solubility, Molal	
	KNO_3	Mixt.[a]
450°	0.011	0.071
510°	0.034	0.073
530°	0.045	0.073
550°	0.059	0.075

[a] 50 grams KNO_3 + 6 grams KBr.

The relationship between bromide found and bromide ion concentration in the molten KNO_3 for this method can also be derived using the constants K_1, K_2 and K_{sp}. Let the bromide found by this method be (Br). Then:

$$(Br) = \text{total Br} - Ag$$

$$(Br) = [Br^-] + [AgBr] + 2[AgBr_2^-] - [Ag^-] - [AgBr] - [AgBr_2^-]$$

$$(Br) = [Br^-] - [Ag^+] + [AgBr_2^-]$$

$$[Br] = (Br) + (K_{sp}/[Br^-]) - K_1K_2K_{sp}[Br^-]$$

$$[Br] = \frac{(Br) \pm [(Br)^2 + 4K_{sp}(1 + K_1K_2K_{sp})]^{1/2}}{2\,(1 + K_1K_2K_{sp})}$$

When (Br) was more than 0.2*m*, this equation simplified to:

$$[Br^-] = \frac{(Br)}{1 + K_1K_2K_{sp}}$$

RESULTS

The distribution coefficient for thallium:

$$K_o = (Tl^- + TlBr)_{KNO_3}/(TlBr)_{AgBr}$$

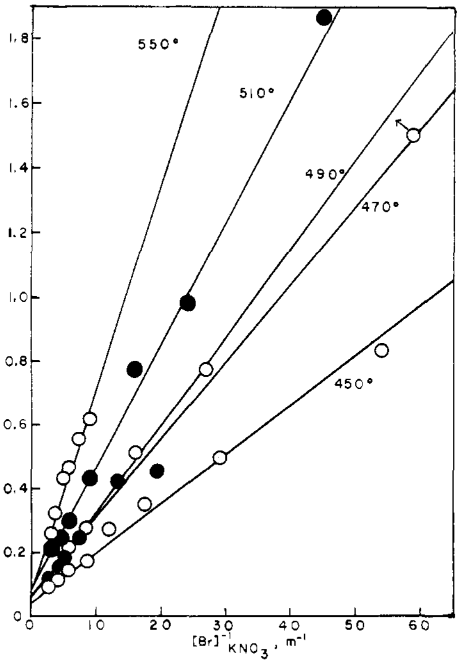

Figure 1. Distribution of thallium bromide between KNO_3 and AgBr

was measured in a series of experiments in which varying amounts of KBr were added. The results of these series at 450°, 470°, 490°, 500°, 510°, 530°, and 550° C. are given in Table II and shown in Figure 1.

The constants for Equation 1 relating observed distribution coefficient and bromide ion concentration were determined by the method of least squares. The Y intercept (K) and the slope (K/k) are given in Table II. Probable errors were determined from the residuals.

The distribution constant, K, was:

$$K = [\mathrm{TlBr}]_{\mathrm{KNO_3}}/[\mathrm{TlBr}]_{\mathrm{AgBr}}$$

Table II indicates that K increased slightly with increasing temperature, although the increase was not much greater than the probable error. Since the distribution constant is approximately the ratio of the solubilities, these results indicate that the heats of solution of TlBr in these two solvents must be nearly equal.

The association constant, k, was equal to the intercept divided by the slope. The slope increased markedly with increasing temperature which indicated that the association constant was decreasing over this temperature range. Since there was a high probable error in calculating the small intercept value, averaged values of K were used to calculate

Table II. The Distribution of Thallium Between KNO_3 and AgBr

Tl Found, Mg. TlBr/Gram Solvent: KNO_3	AgBr	Total, mg.	K_o	KBr Added, Grams	Total Br, Molal	$[Br^-]$ Molal	$[Br^-]^{-1}$ Molal^{-1}
450° C.							
4.65	5.55	509	0.837	0.2	0.026	0.018	54^a
3.36	6.73	507	0.500	0.5	0.0466	0.034	29^a
2.38	6.68	457	0.356	1.0	0.0752	0.057	17.4
2.01	7.24	470	0.277	1.5	0.107	0.083	12.0
1.45	8.43	503	0.172	2.0	0.147	0.115	8.68
1.20	8.05	476	0.149	3.0	0.220	0.174	5.75
0.98	8.53	494	0.114	4.0	0.292	0.232	4.31
0.794	8.14	474	0.097	6.0	0.461	0.369	2.71
$K_{sp} = 6 \times 10^{-5}$ $K_1 = 73$ $K_2 = 30$ $K = 0.039$ $K/k = 0.0183$ $P_K = 0.009$ $P_{K/k} = 0.0009$							
470° C.							
3.23	7.11	520	0.455	0.5	0.055^b	0.052	19.2
2.60	6.08	500	0.428	1.0	0.084^b	0.076	13.1
1.84	7.52	478	0.245	2.0	0.154^b	0.135	7.41
1.50	8.23	500	0.183	3.0	0.263	0.198	5.04
1.21	7.96	478	0.152	4.0	0.294	0.222	4.51
1.00	8.10	483	0.123	6.0	0.443^b	0.384	2.60
$K_{sp} = 1 \times 10^{-4}$ $K_1 = 64$ $K_2 = 24$ $K = 0.075$ $K/k = 0.0220$ $P_K = 0.020$ $P_{K/k} = 0.0019$							
490° C.							
					Total Br – AgBr, Molal		
6.06	4.01	503	1.52	0.0	0.010	0.017	59.8^a
3.98	5.12	456	0.778	0.5	0.039	0.037	27.0
3.03	5.93	453	0.512	1.0	0.073	0.063	15.9
1.96	7.13	464	0.275	2.0	0.139	0.116	8.62
1.73	7.98	500	0.217	3.0	0.207	0.171	5.85
1.41	8.15	498	0.173	4.0	0.282	0.232	4.31
$K_{sp} = 2 \times 10^{-4}$ $K_1 = 56$ $K_2 = 20$ $K = 0.057$ $K/k = 0.0271$ $P_K = 0.010$ $P_{K/k} = 0.0006$							
500° C.							
2.57	7.18	494	0.358	1.5	0.109	0.091	11.0
2.08	7.53	491	0.276	2.0	0.144	0.118	8.48
2.01	7.81	503	0.257	2.5	0.173	0.141	7.10
1.69	7.92	495	0.213	3.0	0.210	0.171	5.85
1.51	8.10	499	0.187	4.0	0.282	0.228	4.39
1.30	8.21	494	0.158	5.0	0.352	0.284	3.52
1.24	8.10	496	0.153	6.0	0.428	0.345	2.90
$K_{sp} = 2.5 \times 10^{-4}$ $K_1 = 54$ $K_2 = 18$ $K = 0.073$ $K/k = 0.0252$ $P_K = 0.005$ $P_{K/k} = 0.0008$							
510° C.							
3.86	2.06	296^c	1.87	0.0	0.013	0.022	45.5^a
4.16^d	4.24	504	0.982	0.5	0.042	0.041	24.4
3.47^d	4.46	500	0.778	1.0	0.071	0.062	16.1
2.48^d	5.73	501	0.432	2.0	0.131	0.109	9.18
1.99^d	6.70	530	0.297	3.0	0.196	0.162	6.18
1.65^d	6.70	517	0.247	4.0	0.253	0.207	4.83
1.38^d	6.58	500	0.210	6.0	0.384	0.312	3.20
$K_{sp} = 3 \times 10^{-4}$ $K_1 = 50$ $K_2 = 15$ $K = 0.079$ $K/k = 0.0387$ $P_K = 0.021$ $P_{K/k} = 0.0017$							

(*Continued on page 98*)

Table II. The Distribution of Thallium Between KNO_3 and AgBr (*Continued*)

Tl Found, Mg. TlBr/Gram Solvent							
KNO_3	AgBr	Total, mg.	K_o	KBr Added, Grams	Total Br, Molal	$[Br^-]$ Molal	$[Br^-]^{-1}$ Molal^{-1}
530° C.							
2.36	6.42	441	0.367	1.5	0.112	0.102	9.80
2.07	6.48	436	0.320	2.0	0.148	0.131	7.65
1.78	6.75	437	0.264	2.5	0.181	0.157	6.36
1.60	6.75	431	0.237	3.0	0.218	0.188	5.32
1.37	6.92	432	0.198	4.0	0.290	0.248	4.03
1.27	7.20	444	0.177	5.0	0.364	0.310	3.23
1.17	7.60	465	0.154	6.0	0.437	0.370	2.70
$K_{sp} = 4 \times 10^{-4}$ $K_1 = 45$ $K_2 = 10$ $K = 0.076$ $K/k = 0.0303$ $P_K = 0.005$ $P_{K/k} = 0.0007$							
550° C.							
3.30	5.34	440	0.619	1.5	0.124	0.112	8.94
2.93	5.29	420	0.553	2.0	0.156	0.138	7.25
2.53	5.41	407	0.468	2.5	0.194	0.170	5.89
2.39	5.44	400	0.438	3.0	0.228	0.199	5.02
1.90	5.93	407	0.320	4.0	0.299	0.259	3.86
1.73	6.50	436	0.266	5.0	0.372	0.322	3.11
$K_{sp} = 6 \times 10^{-4}$ $K_1 = 40$ $K_2 = 7$ $K = 0.094$ $K/k = 0.0615$ $P_K = 0.021$ $P_{K/k} = 0.0036$							

[a] These results were not used in least squares calculations because the uncertainty in bromide concentration was much greater than in the other experiments. Points are shown in Figure 1. [b] Method 2; total Br − AgBr. [c] 301 mg. used in this experiment. [d] 60 gram KNO_3 and 60 gram AgBr used in these experiments.

the association constant from the slope and intercept. The values of k decreased from 2.6 (moles/kg.)$^{-1}$ at 450° C. to 1.9 at 550° C. The heat of association could be estimated from the slope of the log plot of the averaged k values *vs.* $1/T$. ΔH was -6.0 ± 0.4 kcal. A negative heat of association has been found for most halides in fused nitrates.

Braunstein determined the association constant for TlBr from e.m.f. measurements and reported the value 31 (mole ratio units) at 240° C. in equimolar $NaNO_3$-KNO_3 (*1*). From the temperature dependence, Braunstein estimated the association constant to be 15 to 20 at 450° C. The change from $NaNO_3$-KNO_3 to KNO_3 will affect this estimate somewhat; Hill, Braunstein, and Blander (*2*) reported that the first association constant for silver chloride in $NaNO_3$ was 176 at 402° C. while in KNO_3, it was 396 at 402° C. The association constant reported here (26 on a mole ratio basis) agrees with the constant determined from e.m.f. measurements. This, then, is another example of agreement between different physical methods for the determination of association constants in fused salts.

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