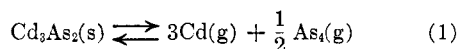


small pieces, was sealed in an evacuated quartz tube. The  $\text{CdAs}_2$ , located at one end of the tube, was then heated to various temperatures while dew-points were observed at the opposite end of the tube in an independently controlled furnace. The use of an infrared lamp in the manner described above was the only difference between the technique used here and that used for  $\text{ZnAs}_2$ . Dew-point measurements were carried out on two samples in the temperature range 334 to 615°. The data, which are presented graphically in Fig. 2, were taken with both increasing and decreasing  $\text{CdAs}_2$  temperature.

Measurements of the dissociation pressure of  $\text{CdAs}_2$  were also carried out using the Bourdon gauge. The procedures were the same as those used for  $\text{Cd}_3\text{As}_2$  except that a lower temperature (400°) was used during the outgassing. The results of the measurements are plotted in Fig. 2. A comparison of the two methods shows excellent agreement.

### Discussion

**I.  $\text{Cd}_3\text{As}_2$ .**—A comparison of the vapor pressure data obtained by the two methods shows that the pressures measured by the Bourdon gauge are greater than those calculated from the dew-point experiments by a factor of about 3.6. Since the dew-points were calculated assuming the existence of monomeric  $\text{Cd}_3\text{As}_2$  molecules in the vapor phase, the 3.6:1 ratio between the two sets of data indicates the degree of dissociation of  $\text{Cd}_3\text{As}_2$  in the vapor phase. In order to correct the values of vapor pressure calculated from the dew-points to the values obtained by direct measurement, an average molecular weight of about 129 must be assigned to the gaseous species. Complete dissociation of the compound to monomeric cadmium and tetrameric arsenic would result in an average molecular weight of 135. Therefore, within experimental error, it can be deduced that the compound thermally dissociates according to the reaction



The assumption of monomeric cadmium and tetrameric arsenic is based on data tabulated by Stull

and Sinke.<sup>9</sup> The equilibrium constant for the dissociation represented by equation 1 is

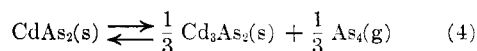
$$K_p = \left(\frac{3.0}{3.5} P\right)^3 \left(\frac{0.5}{3.5} P\right)^{1/2} = 0.24P^{3.5} \quad (2)$$

The vapor pressure data when plotted as  $\log P$  vs.  $10^3/T_{\text{OK}}$  as in curve 2 of Fig. 1 may be represented by the straight line equation

$$\log P_{\text{mm}} = -\frac{6600}{T_{\text{OK}}} + 9 \quad (3)$$

From equations 2 and 3, the heat calculated for the reaction 1 is 106 kcal./mole.

**II.  $\text{CdAs}_2$ .**—The good agreement between the vapor pressures obtained from the two methods shows that the dissociation pressure of  $\text{CdAs}_2$  may be considered in terms of the arsenic pressure only. The pressure contribution from the simultaneous dissociation of  $\text{Cd}_3\text{As}_2$  appears to be negligible. The equilibrium reaction, then, may be written as



and the equilibrium constant for the reaction is

$$K_p' = P_{\text{As}}^{1/3}$$

The experimental data may be represented by the equation

$$\log P_{\text{mm}} = -\frac{7100}{T_{\text{OK}}} + 11 \quad (5)$$

From equation 5 the heat calculated for the reaction 4 is 11 kcal./mole of solid  $\text{CdAs}_2$ .

**Acknowledgments.**—The authors wish to express their thanks to Dr. G. A. Silvey, Dr. T. G. Dunne and Dr. K. Weiser for valuable discussions, and to Mr. C. L. Fisher for constructing the Bourdon gauge.

(9) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," *Advances in Chemistry Series*, No. 8, 1956.

## THE HEAT OF FUSION OF THE ALKALI METAL HALIDES

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The heat of fusion of seventeen alkali halides has been measured by means of a copper block drop calorimeter. The salts and their heats of fusion in kcal. mole<sup>-1</sup> are as follows: LiCl, 4.76; LiBr, 4.22; LiI, 3.50; NaCl, 6.69; NaBr, 6.24; NaI, 5.64; KCl, 6.27; KBr, 6.10; KI, 5.74; RbF, 6.15; RbCl, 5.67; RbBr, 5.57; RbI, 5.27; CsF, 5.19; CsCl, 4.84; CsBr, 5.64; and CsI, 5.64. The heats of fusion are believed to be accurate to at least  $\pm 1$ –2%. Except for the Li salts and, to some slight extent, the sodium salts, the entropy of fusion is constant when the anion varies, but decreases with increasing atomic number of the cation.

In the course of an investigation of the metal-metal halide systems being pursued in this Laboratory, a knowledge of the heat of fusion of the alkali halides became necessary.<sup>2</sup> Many of the heats of fusion listed in a number of commonly used compilations<sup>3a,b</sup> stem from an earlier U. S.

Bureau of Mines compilation.<sup>4</sup> These heats are derived from phase diagrams and at best are averages of widely scattered values; while at their worst are derived from systems now known to be wholly unsuitable for this purpose. As an example, the heat of fusion of LiF as determined calorimetrically at the National Bureau of Standards Miscellaneous Materials: Thermodynamics," National Nuclear Energy Series IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, pp. 196–197. (b) "Selected Values of Chemical Thermodynamic Values," Circular 500, Natl. Bur. Standards (1952).

(4) K. K. Kelley, U. S. Bur. Mines Bulletin 393, 1936.

(1) Work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by the Union Carbide Corporation, Oak Ridge, Tennessee.

(2) M. A. Bredig and H. R. Bronstein, *J. Phys. Chem.*, **64**, 64 (1960).

(3) (a) Leo Brewer, in L. L. Quill, "Chemistry and Metallurgy of

ards was found to be 6,470 cal.,<sup>5</sup> whereas the value accepted before this measurement was 2,360 cal. We, therefore, have measured calorimetrically the heat of fusion of the halides of Li, Na, K, Rb and Cs for which calorimetric data were unavailable.

The method used entailed the measurement of heat content over a sufficient temperature range above and below the melting point of the salt to allow extrapolation to the melting point. A copper block drop calorimeter was chosen as the simplest to build and operate to obtain the desired accuracy. Although it was not deemed necessary to seek the very fine precision now attainable in high temperature heat content measurements, sufficient care was taken in both the design and operation of the calorimeter to ensure heat of fusion values good to approximately 1%.

### Experimental

**Apparatus.**—The calorimeter is essentially of standard design. A gold-plated copper block of 5 in. diameter and 8 in. long supported by three micarta legs is centered in a 6 by 9 in. brass tank which in turn is submerged in a large constant temperature water-bath. The well in the copper block into which the sample container falls is 7 in. deep, the lower 1.5 in. being tapered. A copper gate at the top of the well in contact with the Cu block can be opened just before the container is dropped from the furnace and then closed immediately afterward to prevent loss of heat by radiation.

The sample is equilibrated in a 3.5 in. bore Marshall tube furnace 16 in. long, having ten external taps for the attachment of shunt resistors to help eliminate the temperature gradient. To further reduce gradients, the furnace tube contains a 3.5 in. diameter nickel block 9 in. long, above and below which are lavite insulators. The nickel block sheathes the Inconel tube in which the sample container is held. The 1.2 in. diameter Inconel tube extends 10 in. into the furnace and a sufficient distance below the furnace to bring it just above a similar tube 5 in. long welded to the brass tank. A gate in the Inconel tube just below the furnace lessens heat losses from the furnace. The whole furnace assembly is mounted on a track so that it can be rolled over the copper block immediately preceding a drop and rolled away immediately afterward.

The Inconel sample containers were tapered to fit the taper in the well in the copper block. This, together with the fact that the container bottoms were slightly larger in diameter than that of the bottom of the well, ensured good thermal contact between the container and the copper block.

The temperature of the water-bath around the calorimeter was maintained constant to better than  $\pm 0.001^\circ$  at approximately  $26^\circ$  by means of a thermistor as the temperature-sensitive element in a bridge circuit employing a Speedomax recorder-controller operating an infrared heat lamp external to the bath. The furnace was controlled by a Chromel-Alumel thermocouple which operated a Leeds and Northrup recorder-controller in conjunction with a Leeds and Northrup "DAT" controller. The actual temperature of the sample was measured with a platinum, 90% platinum-10% rhodium thermocouple by means of a Rubicon precision potentiometer. The temperature of the sample container could be maintained to about  $\pm 0.1^\circ$  with the temperature gradient over the height of the container (about  $1\frac{3}{4}''$ ) about  $0.2^\circ$ . The temperature rise of the copper block was measured with a calorimetric type platinum-sheathed platinum resistance thermometer by means of a precision Mueller bridge. The thermometer was imbedded three inches deep in the copper block midway between the well and the outer wall of the block. Temperature differences of  $0.001^\circ$  could be measured.

**Purification of Materials.**—Of the salts used, NaCl, KCl, KBr, KI, CsBr and CsI were Harshaw optical grade single crystals; LiCl, LiBr, LiI, NaBr, NaI, RbF, RbI and CsCl were reagent grade materials; RbCl and RbBr

were made from Rb metal; and CsF was made from CsCl. The Harshaw crystals were taken to be pure and dry except for surface moisture which was removed by pumping. The remaining salts were purified by gradual heating under vacuum to just below their melting temperatures, melting under dry argon, and filtering while molten. Special care was taken with the hygroscopic salts of Li and with CsF in that the corresponding halogen acids were introduced during the very slow heating process to prevent hydrolysis. The dry salts were handled in a dry box and then sealed by welding in the Inconel containers under argon. Upon completion of an experiment, the containers were opened and the salts examined for discoloration, basicity and insoluble material. In no case was a basic solution found. In a very few cases, slight discoloration and a trace of insoluble material were noted. Analysis in these cases showed a few hundredths of a per cent. of Fe, Cr and Ni.

**Experimental Procedure.**—The sample was heated to a known temperature in the furnace, dropped into the copper block, and the temperature rise of the block measured. During the course of the experiment, the sample was allowed to remain in the furnace for varying lengths of time in order to determine an adequate length of time for equilibration with special care being taken for measurements a few degrees above the melting points of the salts. The temperature drift rate of the copper block was measured before and after each drop and extrapolated to an appropriate time during the temperature rise period in order to determine the initial and final temperatures of the copper block.

The heat equivalent of the calorimeter was determined using an N.B.S. sample of synthetic sapphire ( $\text{Al}_2\text{O}_3$ ).<sup>6,7</sup> The experimental procedure was the same as that used for the salts except that the temperature rise of the copper block contributed by the empty container was measured and subtracted from the temperature rise of the container filled with  $\text{Al}_2\text{O}_3$ . Approximately 20-g. samples of  $\text{Al}_2\text{O}_3$  were used. Nine determinations over a temperature range of  $400\text{--}800^\circ$  showed the heat equivalent to be  $1752 \pm 4$  cal./degree rise of the copper block.

For each salt, a minimum of four points over a sixty degree temperature range above the melting point and five points over a one hundred degree range below were measured. Data were obtained to within five to ten degrees of the melting point for both the solid and liquid salts. Premelting was encountered in a number of instances which necessitated the longer range of measurements in the solid region since the data obtained in the premelting zone could not be used in the extrapolation. The salts were always melted before the first drop in any series to ensure intimate contact between the salt and container throughout the measurements. The sample size varied from about 0.1 to 0.25 mole depending on the molar volume of the salts.

### Results and Discussion

The data were plotted as temperature rise of the copper block due to the heat contributed by container plus salt *versus* temperature from which the drop was made. (Small corrections were applied for differences in the final temperature of the copper block.) Straight lines could best represent the data over the relatively short temperature ranges measured. These lines were extrapolated to the melting points of the salts. The difference between the lines for the solid and liquid at the melting point was taken as the temperature rise of the copper block due to the heat of fusion of the salt (the contribution of the container is cancelled out at this point). The product of this value and the heat equivalent of the calorimeter divided by the number of moles of salt was taken as the molar heat of fusion of the salt.

The scatter of the points about the straight lines

(6) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **53**, 593 (1947), RP 1797.

(7) G. T. Furukawa, T. B. Douglas, R. E. McCoskey and D. C. Ginnings, *ibid.*, **57**, 67 (1956), RP 2694.

(5) T. B. Douglas and J. L. Dever, *J. Am. Chem. Soc.*, **76**, 4826 (1954).

TABLE I  
 HEAT AND ENTROPY OF FUSION OF THE ALKALI HALIDES

	$T_m, ^\circ\text{K.}$	$\Delta H_m$ (kcal. mole <sup>-1</sup> )			$\Delta S_m$ (e.u. mole <sup>-1</sup> )		
		This work	Other calorimetric work	Other lit. <sup>3,4</sup>	This work	Other calorimetric work	Other lit. <sup>3,4</sup>
LiF	1121 <sup>5</sup>		6.47 <sup>5</sup>	2.36		5.77	2.1
LiCl	883 <sup>3</sup>	4.76	4.72 <sup>8</sup> , 4.83 <sup>9</sup>	3.20	5.39	5.35, 5.47	3.6
LiBr	823 <sup>3</sup>	4.22		2.90	5.13		3.5
LiI	742 <sup>14</sup>	3.50		1.42	4.72		2.0
NaF	1268 <sup>1</sup>		8.03 <sup>12</sup> , 7.78 <sup>10</sup>	7.00		6.33, 6.14	5.5
NaCl	1073 <sup>1</sup>	6.69	6.85 <sup>10</sup>	7.22	6.23	6.38	6.7
NaBr	1020 <sup>1</sup>	6.24		6.14	6.12		6.0
NaI	933 <sup>1</sup>	5.64		5.24	6.04		5.6
KF	1131 <sup>15</sup>		6.75 <sup>10</sup>	6.50		5.97	5.8
KCl	1043 <sup>15</sup>	6.34	6.27 <sup>8</sup> , 6.10 <sup>10</sup>	6.41	6.08	6.01, 5.85	6.2
KBr	1007 <sup>15</sup>	6.10		5.00	6.06		4.9
KI	954 <sup>15</sup>	5.74		4.10	6.02		4.3
RbF	1068 <sup>16</sup>	6.15	5.49 <sup>11</sup>	4.13	5.76	5.14	3.9
RbCl	995 <sup>17</sup>	5.67		4.40	5.70		4.4
RbBr	965 <sup>17</sup>	5.57		3.70	5.77		3.9
RbI	920 <sup>17</sup>	5.27		2.99	5.73		3.3
CsF	976 <sup>18</sup>	5.19		2.45	5.32		2.6
CsCl	918 <sup>3</sup>	4.84	4.97 <sup>9</sup>	3.60	5.27	5.40	3.9
CBr	909 <sup>3</sup>	5.64		3.00	6.20		3
CsI	899 <sup>18</sup>	5.64		2.50	.27		3

which represent the data was of the order of 0.1%. The actual measured temperature rises of the block ranged from about 1.5 to 3.0° while the differences between the lines for the solid and the liquid at the melting points ranged from about 0.4 to 0.8°. On consideration of the use in the heat of fusion calculations of this difference between two measured larger numbers, the precision of the heat equivalent and heat content measurements, and the small uncorrected systematic errors inherent in the method, the heat of fusion values are believed to be accurate to at least  $\pm 1-2\%$ .

Table I lists the heat and entropy of fusion of all of the alkali halides. The values listed in literature compilations<sup>3,4</sup> are included for comparison with the calorimetric values. Calorimetric values obtained by other investigators are given with those reported in this work. The entropy of fusion was calculated merely by dividing the heat of fusion by the absolute temperature at which the salts melt.

A number of the salts measured in the present work may be compared with values found calorimetrically by other investigators. As can be seen in Table I, Douglas's<sup>8</sup> values for LiCl and KCl and Smith's<sup>9</sup> value for LiCl agree very well with our values. Smith's<sup>9</sup> value for CsCl and Kelley's<sup>10</sup> values for NaCl and KCl are somewhat outside our experimental error. However, the latter two values had been based on heat contents reported to only 3%. Smith's<sup>11</sup> value for RbF is considerably lower than ours, which may be due to the rather large scatter of his heat content data in the vicinity of the melting point. Of the calorimetric measurements not repeated in this work, the values for LiF<sup>5</sup> and NaF<sup>12</sup> are derived from

heat content measurements reported to a high degree of accuracy, whereas the value for KF<sup>10</sup> is based on heat contents reported to 3%.

As has been predicted previously,<sup>13</sup> among the

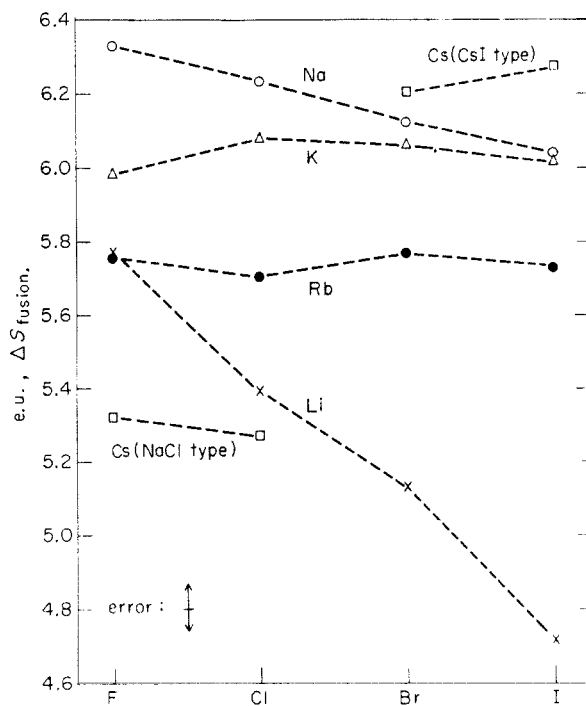


Fig. 1.—Entropy of fusion of the alkali halides.

- (12) C. J. O'Brien and K. K. Kelley, *ibid.*, **79**, 5616 (1957).
- (13) J. W. Johnson, P. A. Agron and M. A. Bredig, *ibid.*, **77**, 2734 (1955).
- (14) J. W. Johnson and M. A. Bredig, unpublished data.
- (15) J. W. Johnson and M. A. Bredig, *THIS JOURNAL*, **62**, 604 (1958).
- (16) O. Schmitz-Dumont and E. Schmitz, *Z. anorg. Chem.*, **252**, 329 (1944).
- (17) I. S. Yaffe and E. R. Van Artsdalen, *THIS JOURNAL*, **60**, 1125 (1956).

(8) T. B. Douglas, Natl. Bur. Standards, private communication.

(9) D. F. Smith, Univ. of Alabama, private communication.

(10) K. K. Kelley, U. S. Bur. Mines Bulletin 476, 1949.

(11) C. E. Kaylor, G. E. Walden and D. F. Smith, *J. Am. Chem. Soc.*, **81**, 4172 (1959).

cesium halides the two groups having different crystal structures, CsF-CsCl (NaCl type) and CsBr-CsI (CsI type), are distinguished by different entropies of fusion, approximately 5.3 and 6.2 e.u. mole<sup>-1</sup>, respectively. The magnitude of the difference as predicted in the above reference was incorrect because the value for the heat of transition of CsCl available at that time was in error. Smith<sup>9</sup> has since measured the heat of transition of CsCl from the CsI structure to the NaCl structure and found it to be 581 cal. mole<sup>-1</sup> at 742.5° K. This corresponds to an entropy of transition of 0.78 e.u. mole<sup>-1</sup>, of the same order as the difference in the entropy of fusion of the two groups of cesium halides.

The spread in the entropy of fusion of the alkali halides evident in the older erroneous values is considerably reduced in the present data. Definite trends in the data have now become obvious (Fig. 1). There is a trend in the Li salts for the entropy of fusion to decrease from 5.8 e.u. in LiF to 4.7 e.u. in LiI, while in the other salts, the entropy of fusion remains essentially constant with an increase in *anion* size. However, a residue of the effect noticeable in the Li salts is still apparent

(18) M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *J. Am. Chem. Soc.*, **77**, 1454 (1955).

in the sodium salts. In another trend, with an increase in the size of the *cation*, the entropy of fusion decreases from that for NaF and NaCl of approximately 6.3 to 5.3 e.u. for CsF and CsCl. The entropy curve for the Li salts appears to be displaced downwards by 1 to 2 e.u. It may be significant that, excepting the Li salts, the anion and cation affect the entropy of fusion in a differing manner. The heats of fusion, on the other hand, show a decrease with an increase of the size of either the cation (except Li) or the anion. CsBr and CsI with their different crystal structure are, of course, excluded from the above considerations. As the entropy of melting is relatively constant for the salts of NaCl type structure ( $\Delta S_m$  average =  $5.75 \pm 0.30$  e. u. mole<sup>-1</sup>), it follows that a plot of the heats of fusion bears great resemblance to a plot of the melting points which has been discussed from various points of view.<sup>19a,b</sup>

**Acknowledgment.**—We wish to acknowledge the assistance of D. E. Lavelle of this Laboratory, who prepared the samples of the anhydrous salts used in this work.

(19) (a) K. Fajans, "Radioelements and Isotopes. Chemical Forces and Optical Properties of Substances," McGraw-Hill Book Co., New York, N. Y., 1931 p. 66; (b) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca N. Y., 1939.

## NOTES

### A REMEASUREMENT OF THE SELF-DIFFUSION COEFFICIENTS OF IODIDE ION IN AQUEOUS SODIUM IODIDE SOLUTIONS

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The self-diffusion of iodide ions in the solutions of alkali metal iodides has been investigated by Mills and Kennedy,<sup>1</sup> Friedman and Kennedy,<sup>2</sup> and by Wang and Kennedy.<sup>3</sup> The open-ended capillary method, introduced by Anderson and Saddington<sup>4</sup> and modified by Wang<sup>5</sup> has been used for the measurements in HI, LiI, KI, RbI and CsI. The usual plot  $D$  vs.  $\sqrt{c}$  showed a close similarity of the behavior of I<sup>-</sup> in these five iodides: as the concentration of electrolyte increased,  $D$  was regularly decreasing from the Nernst limiting value corresponding to infinite dilution.

The self-diffusion of I<sup>-</sup> in NaI solutions, at 25°, has not been studied with the same method. Wang and Kennedy have used a free diffusion method, where the diffusion process took place from one capillary into a second identical one,

pressed against the first capillary. This technique has not been used any more after this first trial, and other authors have criticized it.

As the results found by Wang and Kennedy were different from those corresponding to the other alkali iodides, and as there is no apparent reason why NaI should behave in a singular way, it seemed of interest to remeasure the self-diffusion coefficients of the iodide ion in sodium iodide solutions, using the open-ended capillary method.

#### Experimental

We have used a type of diffusion cell which is different from the one described by Wang, and applied no stirring. Details of the apparatus and manipulations are to be found in a preceding paper.<sup>6</sup>

The radioactive solutions were prepared by adding 5  $\mu$ l. of a carrier-free <sup>131</sup>I solution (specific activity = 5 mc./ml.) provided by the Isotope Division, A.E.R.E., Harwell, England, to 10 ml. of the sodium iodide solutions. The diffusion times were of 4 to 5 days.

#### Results and Discussion

The self-diffusion coefficients of I<sup>-</sup> in aqueous NaI solutions, at 25°, have been measured over the range 10<sup>-4</sup> to 4 *M*. The results are listed in Table I, and the plot of  $D$  vs.  $\sqrt{c}$  is represented in Fig. 1. We reproduce also, for comparison purposes, the curve of Wang and Kennedy.

Each value reported in Table I is the average value of 3 to 4 measurements, and the error quoted

(1) R. Mills and J. W. Kennedy, *J. Am. Chem. Soc.*, **75**, 6596 (1953).

(2) A. M. Friedman and J. W. Kennedy, *ibid.*, **77**, 4499 (1955).

(3) J. H. Wang and J. W. Kennedy, *ibid.*, **72**, 2080 (1950).

(4) J. A. Anderson and K. Saddington, *J. Chem. Soc.*, S381 (1949).

(5) J. H. Wang, *J. Am. Chem. Soc.*, **73**, 510 (1951).

(6) E. Berne and M. J. Weill, *THIS JOURNAL*, **64**, 258 (1960).