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ENTHALPIES AND HEAT CAPACITIES OF SOLID
MOLYBDENUM FLUORIDE MIXTURES

W. D. Powers
G. C. Blalock

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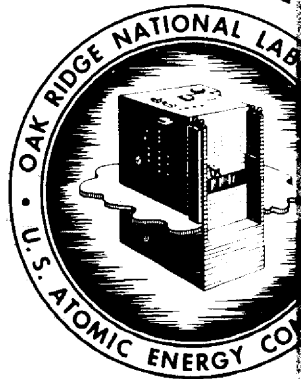


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ENTHALPIES AND HEAT CAPACITIES OF SOLID
AND MOLTEN FLUORIDE MIXTURES

by

W. D. Powers
G. C. Blalock

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SUMMARY

The enthalpies and heat capacities of seventeen fluoride mixtures in the liquid state have been determined using Bunsen Ice Calorimeters and copper block calorimeters. The fluoride mixtures were composed of the fluorides of two or more of the following metals: lithium, sodium, potassium, beryllium, zirconium, and uranium. The enthalpies and heat capacities of most of these mixtures were studied in the solid state also. Estimates of the heat of fusion have been made. General empirical equations have been developed which represent the enthalpies and heat capacities of the fluoride mixtures in the liquid and in the solid state.

INTRODUCTION

For a number of years the enthalpies and heat capacities of various fluoride mixtures have been determined by the ORNL Physical Properties Group for the purpose of predicting the heat transfer characteristics of these mixtures. This report is a compilation of the data previously reported in the form of memoranda. Equations have been formulated so that the enthalpy and heat capacity may be predicted from the composition.

In a sense this is a progress report since these properties are being determined presently for other fluoride salt mixtures.

EXPERIMENTAL METHOD

Samples of the fluorides heated to constant and uniform temperatures were dropped into calorimeters. The differences between the heat contents of the samples at the furnace temperature and at the final temperature of the calorimeter were measured by the calorimeters. The derivative of the enthalpy with respect to temperature yielded the heat capacity.

The design of the furnaces and of the Bunsen Ice Calorimeters has been described previously (1,2). A full description of the Copper Block Calorimeter will be given in a forthcoming ORNL report. During this investigation both apparatuses have been modified from time to time. The brief descriptions which follow describe the apparatuses used at present.

The samples of the fluorides were contained in tapered metal capsules, 2 1/2 inches long and 1 1/4 inches average diameter. The capsules were sealed by heliarc welding in an inert gas filled drybox to avoid possible contamination with water, oxygen, and carbon dioxide.

Capsules containing the samples were heated in 6 inch long silver liners centered in tube furnaces 24" long. The temperatures of the furnaces were measured by platinum - platinum-rhodium thermocouples located in the silver liners and were held at the desired level by "Simplex" controllers. After the capsules had reached the temperature of the furnace, they were dropped into the calorimeters by electrically fusing

the short pieces of wire on which they were suspended in the furnaces. This process of heating a sample and dropping it into the calorimeter will subsequently be referred to by the descriptive work "drop".

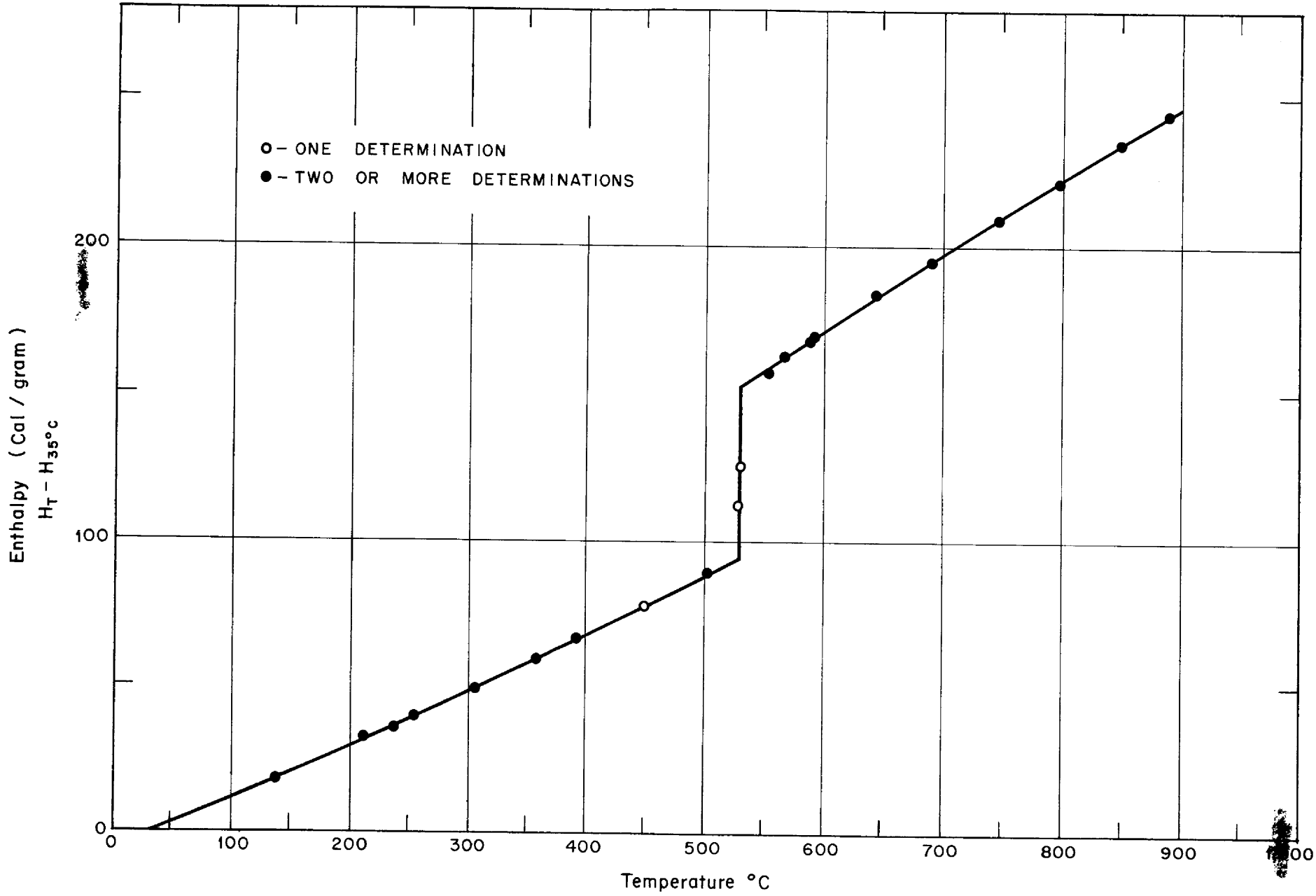
In the Bunsen Ice Calorimeter the heat liberated by the sample in cooling from the temperature of the furnace to that of the calorimeter melted some of the ice in an ice-water mixture. The change from ice to water was accompanied by a volume change which was measured by a system of burets connected to the calorimeter. Each milliliter change was equivalent to 878.7 calories.

The total amount of heat measured by the ice calorimeters varied from 1,000 to over 30,000 calories. It was found that the precision of the measurements was significantly less when large amounts of heat were liberated. Although the ice calorimeter is in general a very precise device (3,4), it is felt that when large amounts of heat are liberated, a non-isothermal state can exist giving rise to poorer precision. A copper block calorimeter was developed to remedy this difficulty; it was found that this new calorimeter was characterized by far greater precision when high quantities of heat were released than was the case for the ice calorimeter. Two copper block calorimeters were placed into regular service, which now yield data at a relatively high rate.

In the copper block calorimeter the heat liberated by the sample heated a large mass of copper. The temperature rise of the copper was measured by an iron-constantan thermopile (12 junctions in the copper and 12 junctions in an ice bath). The copper block was contained in a stainless steel shell which was submerged in a water bath. A potentiometer controller activated by another thermopile maintained a zero temperature difference between the copper block and the water bath to minimize any heat exchange between the copper block and its surroundings. The copper block was calibrated in terms of calories per millivolt by making "drops" with aluminum oxide. The enthalpy of aluminum oxide is well known (4). The precision of the calibration is within $\pm 0.5\%$.

The least squares method was used to determine an equation which represented the experimental data. The enthalpy determinations made using the ice calorimeters exhibited enough scatter so that only a linear relationship between the enthalpy and temperature was found to be significant; therefore, the reported heat capacities were not temperature dependent. But the more precise results obtained with the copper block calorimeter could be represented by a definite quadratic relationship. Thus the heat capacity was temperature dependent.

The individual experimental enthalpy values that were obtained using a copper block calorimeter for the drops of mixture No. 70 are listed in Table 6 and are shown in Figure 1. The results are typical of those obtained with the ORNL copper block calorimeter.



Temperature Vs Enthalpy, Mixture No 70
Fig 1

EXPERIMENTAL RESULTS

The enthalpy and heat capacity equations obtained are listed in Table 2. The type of calorimeter used, the enthalpy and heat capacity together with the temperature range over which these properties were studied, and the heat of fusion at the reported melting point (5)(6) are shown in this table.

The enthalpies and heat capacities of a few salt mixtures have been determined by other laboratories. A comparison between the results obtained at ORNL and the outside laboratories are listed in Table 1. At the National Bureau of Standards (7) the enthalpy of mixture No. 12 in the liquid state between 454° and 900°C was found to be

$$H_T - H_{0^\circ\text{C}} = 15.0 + 0.4910T - 4.63 \times 10^{-5}T^2 \text{ cal./g.}$$

and for mixture No. 40 in the liquid state between 520° and 900°C.

$$H_T - H_{0^\circ\text{C}} = 4.2 + 0.3137T - 3.765 \times 10^{-5}T^2 \text{ cal./g.}$$

At the Naval Research Laboratory (8) the enthalpy of mixture No. 12 in the solid state between 30° and 455°C was found to be

$$H_T - H_{30^\circ\text{C}} = -7.99 + 0.264T + 7.25 \times 10^{-5}T^2 \text{ cal./g.}$$

and in the liquid state between 455° and 900°C

$$H_T - H_{30^\circ\text{C}} = -32.98 + 0.7278T - 4.962 \times 10^{-4}T^2 \\ + 0.381 \times 10^{-6}T^3 - 1.199 \times 10^{-10}T^4 \text{ cal./g.}$$

In Table 1 7.99 cal. has been added to the enthalpies determined by the Naval Research Laboratory so that all enthalpies would have the same base temperature of 0°C.

TABLE 1

Checks with Other Laboratories
 Enthalpies cal./g.
 Heat Capacities cal./g. °C

Mixture No. 12

Temperature °C	ORNL Ice Calorimeter		NBS		NRL	
	$H_T - H_{O^{\circ}C}$	c_p	$H_T - H_{O^{\circ}C}$	c_p	$H_T - H_{O^{\circ}C}$	c_p
100	25.5	.29			27.1	.278
200	55.5	.31			55.7	.293
300	87.5	.33			85.7	.308
400	121.5	.35			117.2	.322
500	256.8	.45	248.9	.445	255.0	.457
600	302.1	.45	292.9	.435	299.8	.440
700	347.4	.45	336.0	.426	343.2	.429
800	392.7	.45	378.2	.417	385.6	.420
900	438.0	.45	419.4	.408	427.2	.411
H_{fusion}	95.4		---		99.0	

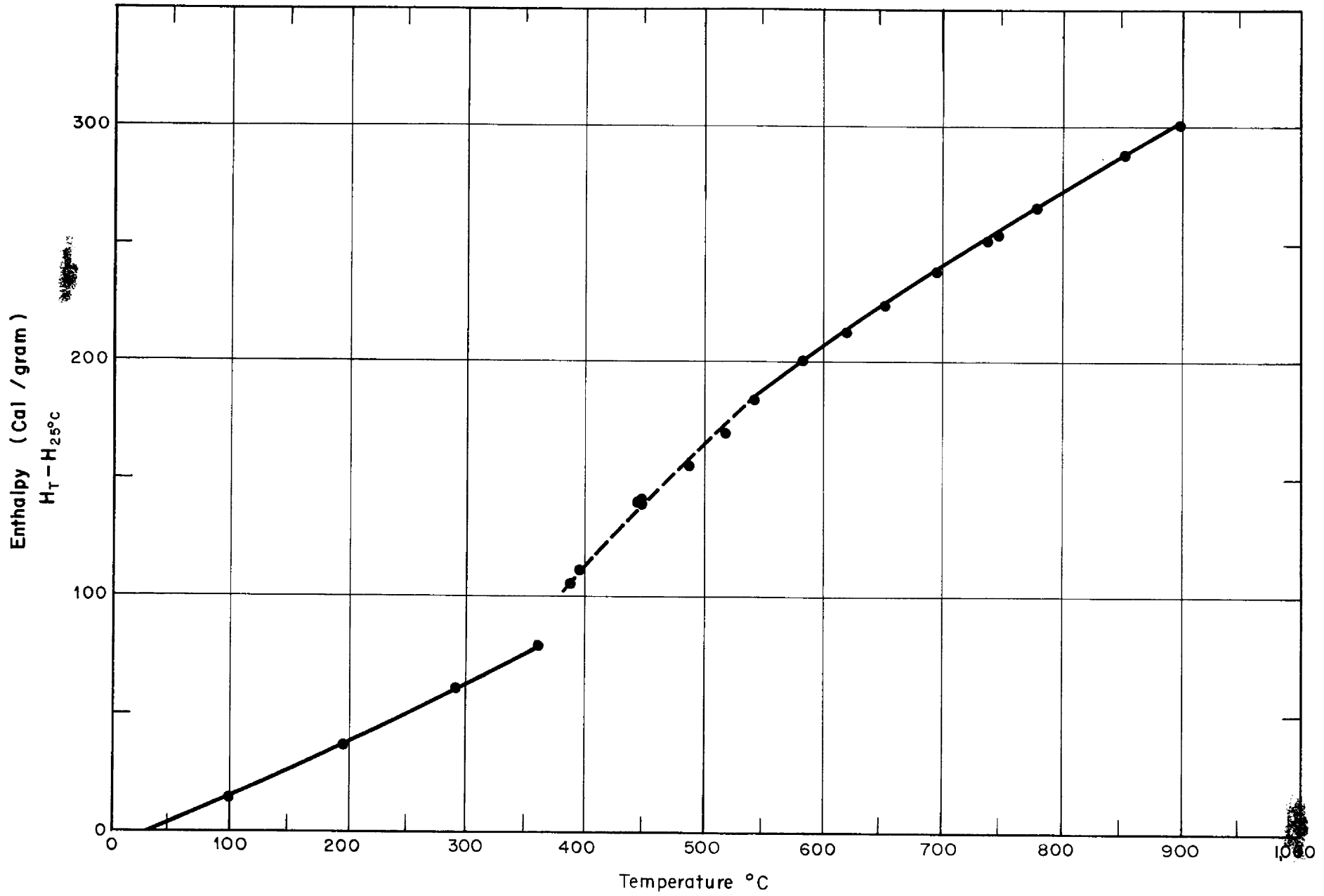
Mixture No. 40

Temperature °C	ORNL Copper Block		NBS		ORNL Ice Calorimeter	
	$H_T - H_{O^{\circ}C}$	c_p	$H_T - H_{O^{\circ}C}$	c_p	$H_T - H_{O^{\circ}C}$	c_p
600	178.7	.266	178.9	.269	182.7	.25
700	205.2	.266	205.3	.261	207.5	.25
800	231.8	.266	231.1	.253	232.3	.25
900	258.3	.266	256.0	.246	257.0	.25

The comparison shown indicates that the enthalpies obtained at ORNL with the ice calorimeter differ from those of the other laboratories by a maximum of 5%, and heat capacities differ by a maximum of 10%. Only one comparison is available for the ORNL copper block calorimeter. The enthalpies deviate with a maximum of 1%. At 700°C the heat capacity differed by 2%; at the extremes in the temperature range studied (the melting point and 900°C) the heat capacity difference was as great as 8%.

Most of the mixtures studied were near eutectic composition, and melting took place isothermally or over a very narrow temperature range. One mixture, No. 82, melted over a wide range of temperature ($\sim 375^{\circ}$ to 545°C), Figure 2. This was a zirconium fluoride base mixture. The enthalpy of the liquid compared favorably with the enthalpies in the liquid state of the other zirconium base mixtures (Table 4). This indicated that there was a heat of fusion similar in value to the other mixtures which was absorbed in the melting process. Mixture No. 21 did not exhibit an isothermal melting. This mixture was not studied in detail below the reported melting point. The melting behavior is believed similar to No. 82. The enthalpy of the liquid was similar to the values of the other zirconium fluoride mixtures.

One mixture, No. 3, containing 60 M% BeF_2 , exhibited a glass-like behavior. The BeF_2 mixtures resembled those of heat capacities (slopes of enthalpy temperature curves) of the alkali fluoride mixtures. However, the enthalpy of No. 3 in the liquid state is much lower than the liquid enthalpies of the other mixes (Table 5). Presumably there is little, if any, heat of fusion.



Temperature Vs Enthalpy, Mixture No 82
Fig 2

DISCUSSION OF RESULTS

It is of interest to find general relationships between the enthalpies and heat capacities of the various fluorides. For most of the solid elements the heat capacity at constant volume is equal to $3R$ or $6 \text{ cal./}^\circ\text{C}$ per gram atom. The more modern theories of Einstein and Debye have the same value as a limit which is reached at normal temperatures for most elements (9). At constant pressure the heat capacities are found to be greater, being about $6.4 \text{ cal./}^\circ\text{C}$ per gram atom (Dulong and Petit's law). The Debye equation also predicts correctly the heat capacity of some compounds, these being the compounds that crystallize in the cubic system. The equation may be modified to predict compounds that do not crystallize in the cubic lattice. In 1865 Kopp suggested that the molar heat capacity of a compound is approximately equal to the sum of the atomic heat capacities of its constituent elements.

In the case of liquid compounds which have no definite groups of atoms or radicals, it has been found empirically that each gram atom contributes approximately $8 \text{ cal./}^\circ\text{C}$ to the molar heat capacity of the compound (10). In general if there are definite groupings of atoms (such as in the $\text{SO}_4^{=}$ and OH^- ions), the average heat capacity will be less. In the case of the hydroxides the average heat capacity in the liquid state is $7.0 \text{ cal./g. atom } ^\circ\text{C}$ (2).

In order to find the contribution per gram atom the average molecular weight and the average number of atoms per mixture are needed. The average molecular weight has been successfully used in correlating the densities of the liquid fluoride mixtures (11). The quantities are defined as follows:

$$\bar{M} = \sum_i x_i M_i$$

$$\bar{N} = \sum_i x_i N_i$$

where \bar{M} = average molecular weight of mixture

\bar{N} = average number of atoms per mixture

M_i = molecular weight of component

N_i = number of ions per component

x_i = mole fraction of component

When the enthalpy of a mixture in units of calories per gram is multiplied by \bar{M}/\bar{N} the product is the enthalpy per gram atom. The heat capacity per gram atom may be found in the same way. Table 3 lists the heat capacities per gram atom of all the mixtures investigated together with the values of \bar{M} , \bar{N} , and \bar{M}/\bar{N} .

Figure 3 shows the relationship between the heat capacity in gram units in the liquid state and the factor \bar{M}/\bar{N} . In this figure with the logarithmic scales the straight lines drawn represent the equation

$$(\bar{M}/\bar{N})(c_p) = \text{const} = C_p$$

where c_p = heat capacity, cal./g. °C

C_p = heat capacity, cal./g. atom °C

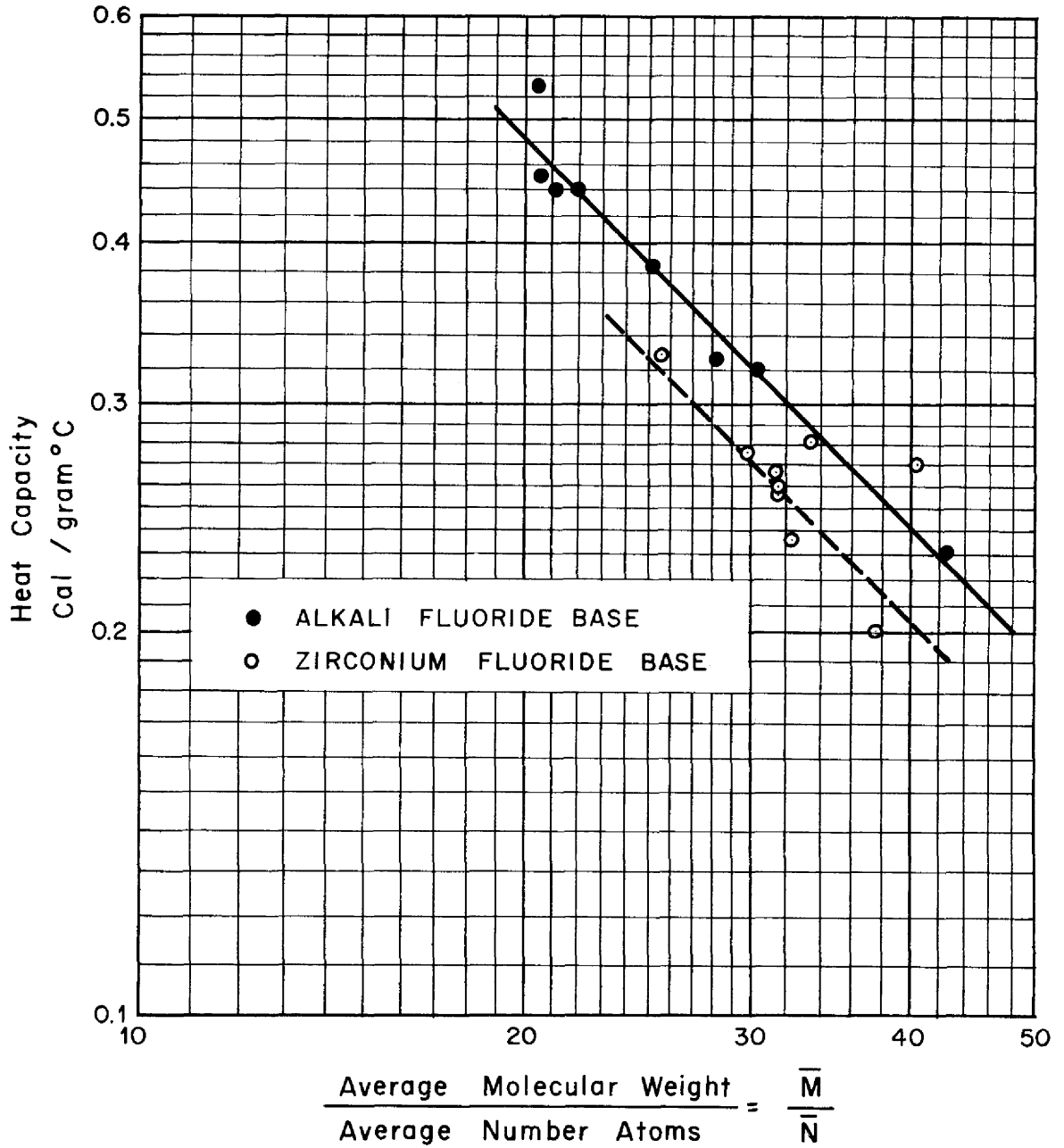


Fig 3

The fluoride mixtures may be correlated best by dividing them into two groups: those that contain zirconium fluoride, and those that do not. The latter will be referred to as the alkali fluoride mixtures.

Zirconium Fluoride Mixtures

The enthalpies in cal./g. atom of the zirconium base mixtures are listed in Table 4. Most of the mixtures studied in this group consist of sodium and zirconium fluorides with a little or no uranium fluoride. The following equations were developed to represent these mixtures (Nos. 30, 31, 40, 44, 70).

In the solid

$$\begin{aligned} \underline{H}_T - \underline{H}_{25^\circ\text{C}} &= -123 + 5.37T + 0.81 \times 10^{-3}T^2 & (1) \\ C_p &= 5.37 + 1.62 \times 10^{-3}T \\ &= 5.86 \text{ at } 300^\circ\text{C} \end{aligned}$$

and in the liquid

$$\begin{aligned} \underline{H}_T - \underline{H}_{25^\circ\text{C}} &= 104 + 9.51T - 1.0 \times 10^{-3}T^2 & (2) \\ C_p &= 9.51 - 2.0 \times 10^{-3}T \\ &= 8.11 \text{ at } 700^\circ\text{C} \end{aligned}$$

The enthalpies calculated by these equations are also listed in Table 4. The enthalpies of Nos. 30, 31, 40, 44, 70 are represented by these equations to within 2% and all the zirconium fluoride base materials to within 10%. The heat capacity of all zirconium fluoride base materials are represented to within 15% except for Mixture No. 33, with a heat capacity of

10.9 cal./g. atom °C. The cause of the high heat capacity of this mixture is unknown. Since the temperature range in which this mixture was studied in the liquid state was small (610° - 930°C) and therefore subject to more error, it is planned to check the enthalpy of this mixture with the more accurate copper block calorimeter.

The heat of fusion of these mixtures varied between 1570 to 2040 calories per gram atom with an average of 1810 cal.

Alkali Fluoride Mixtures

The enthalpies in cal./g. atom of the alkali fluoride base mixtures are listed in Table 5. Most of mixtures studied consist of alkali fluorides with uranium fluoride. Two mixtures contain beryllium fluoride. The following equations represent all these mixtures.

In the solid,

$$\underline{H}_T - \underline{H}_{25^\circ\text{C}} = -340 + 6.76T \quad (3)$$

$$C_p = 6.76$$

and in the liquid

$$\underline{H}_T - \underline{H}_{25^\circ\text{C}} = \Delta H_f - 1610 + 9.47T \quad (4)$$

$$C_p = 9.47$$

Because the heat of fusion varied greatly (from 0 to 1970 cal./g. atom) the heat of fusion had to be included in the equation representing the liquid to give a satisfactory correlation. The enthalpies calculated by these equa-

tions are also listed in Table 5. For the solid state the enthalpies calculated by the equations from 200°C and higher agreed within 10% except for Mixture No. 3 at 300°C. This is the mixture that indicated formation of a glass and therefore would be expected to deviate from the others. The heat capacities of the solid agreed within 6% of the equation. In the liquid the enthalpies observed agreed within 5% and the heat capacities within 16%.

FUTURE WORK

- I. The ORNL Physical Properties Group has suggested that the presence of complex compounds might increase the heat capacity of the liquid. If these complex compounds should be decomposed between the melting point and the upper temperature at which the liquid will be used, the heat required for decomposition would increase the heat capacity of the liquid. At present various mixtures in the sodium fluoride-zirconium fluoride system are being measured to determine the relationship between heat capacity and composition. Complex compounds are known to exist in the solid state in this system.
- II. The heat capacity of mixture No. 33 which is at variance to the other zirconium fluoride mixtures will be measured using the more accurate copper block calorimeter.
- III. As new mixtures are developed, their enthalpies and heat capacities will be determined.

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TABLE 2
Enthalpies and Heat Capacities

Mixture	Calorimeter	Temperature °C	Enthalpy = $H_T - H$ (cal./g.) Heat Capacity = c_p (cal./g. °C) Heat of Fusion = ΔH_f (cal./g.)	Memo by: W. D. Powers G. C. Blalock
1	Ice	250°-465°	Solid $H_T - H_{0°C} = -5 + 0.219T$ $c_p = 0.22$	CF 51-11-195
		480°	Fusion $\Delta H_f = 21$	
		520°-990°	Liquid $H_T - H_{0°C} = -35 + 0.325T$ $c_p = 0.32$	
2	Ice	240°-480°	Solid $H_T - H_{0°C} = -1 + 0.149T$ $c_p = 0.15$	CF 51-9-64
		530°	Fusion $\Delta H_f = 30$	
		540°-1000°	Liquid $H_T - H_{0°C} = -13 + 0.230T$ $c_p = 0.23$	
3	Ice	280°-1050°	Glass $H_T - H_{0°C} = -43 + 0.315T$ Liquid $c_p = 0.32$	CF 51-11-195
12	Ice	60°-454°	Solid $H_T - H_{0°C} = -2.6 + 0.271T + 9.8 \times 10^{-5}T^2$ $c_p = 0.27 + 19.6 \times 10^{-5}T$ $= .330$ at 300°C	CF 54-5-160
		454°	Fusion $\Delta H_f = 95$	
		475°-875°	Liquid $H_T - H_{0°C} = 30.3 + 0.453T$ $c_p = 0.45$	

TABLE 2 (Con't.)

Mixture	Calorimeter	Temperature	Enthalpy = $H_T - H$ (cal./g.) Heat Capacity = c_p (cal./g. °C) Heat of Fusion = ΔH_f (cal./g.)	Memo by: W. D. Powers G. C. Blalock
14	Ice	90°-450°	Solid $H_T - H_{0°C} = -9 + 0.310T$ $c_p = 0.31$	
		452°	Fusion $\Delta H_f = 88$	
		500°-1000°	Liquid $H_T - H_{0°C} = 21 + 0.437T$ $c_p = 0.44$	
21	Ice	510°-890°	Liquid* $H_T - H_{0°C} = -14.5 + 0.277T$ $c_p = 0.28$	CF 52-11-103
30	Ice	340°-500°	Solid $H_T - H_{25°C} = -18.0 + 0.215T$ $c_p = 0.22$	
		520°	Fusion $\Delta H_f = 56$	
		Copper 540°-894°	Liquid $H_T - H_{25°C} = -3.3 + 0.3178T - 4.28 \times 10^{-5}T^2$ $c_p = 0.3178 - 8.56 \times 10^{-5}T$ $= 0.258$ at 700°C	
31	Copper	54°-488°	Solid $H_T - H_{25°C} = -4.4 + 0.1798T + 2.69 \times 10^{-5}T^2$ $c_p = 0.1798 + 5.38 \times 10^{-5}T$ $= 0.196$ at 300°C	CF 55-5-87
		510°	Fusion $\Delta H_f = 60.8$	
		546°-899°	Liquid $H_T - H_{25°C} = -9.8 + 0.3508T - 5.39 \times 10^{-5}T^2$ $c_p = 0.3508 - 10.79 \times 10^{-5}T$ $= 0.275$ at 700°C	
33	Ice	280°-610°	Solid $H_T - H_{0°C} = -17.7 + 0.166T$ $c_p = 0.17$	CF 53-11-128

*See discussion page 12

TABLE 2 (Con't.)

Mixture	Calorimeter	Temperature	Enthalpy = $H_T - H$ (cal./g.) Heat Capacity = c_p (cal./g. °C) Heat of Fusion = ΔH_f (cal./g.)	Memo by: W. D. Powers G. C. Blalock
33	Ice	610°	Fusion $\Delta H_f = 42$	CF 53-11-128
		610°-930°	Liquid $H_T - H_{00C} = -39.0 + 0.270T$ $c_p = 0.27$	
39	Ice	90°-610°	Solid $H_T - H_{00C} = -2.9 + 0.172T$ $c_p = 0.17$	CF 54-8-135
		610°	Fusion $\Delta H_f = 42$	
		653°-924°	Liquid $H_T - H_{00C} = 22.3 + 0.199T$ $c_p = 0.20$	
40	Ice	70°-520°	Solid $H_T - H_{250C} = -4.6 + 0.182T$ $c_p = 0.18$	CF 54-10-140
		520°	Fusion $\Delta H_f = 63$	
	Copper	571°-884°	Liquid $H_T - H_{250C} = 14.8 + 0.2656T$ $c_p = 0.266$	CF 55-5-87
44	Ice	260°-490°	Solid $H_T - H_{00C} = -4.1 + 0.189T$ $c_p = 0.19$	CF 54-5-160
		540°	Fusion $\Delta H_f = 63$	
		590°-920°	Liquid $H_T - H_{00C} = 34.5 + 0.235T$ $c_p = 0.24$	
70	Copper	137°-503°	Solid $H_T - H_{250C} = -2.7 + 0.1596T + 5.15 \times 10^{-5}T^2$ $c_p = 0.1596 + 10.29 \times 10^{-5}T$ $= 0.190$ at 300°	CF 55-5-88
		530°	Fusion $\Delta H_f = 57$	

TABLE 2 (Con't.)

Mixture	Calorimeter	Temperature	Enthalpy = $H_T - H$ (cal./g.) Heat Capacity = c_p (cal./g. °C) Heat of Fusion = ΔH_f (cal./g.)	Memo by: W. D. Powers G. C. Blalock
70	Copper	567°-892°	Liquid $H_T - H_{250C} = 2.2 + 0.3033T - 3.24 \times 10^{-5}T^2$ $c_p = 0.3033 - 6.47 \times 10^{-5}T$ = 0.258 at 700°C	CF 55-5-88
82	Copper	98°-363°	Solid* $H_T - H_{250C} = -9.5 + 0.2304T + 4.07 \times 10^{-5}T^2$ $c_p = 0.2304 + 8.14 \times 10^{-5}T$ = 0.255 at 300°	
		582°-900°	Liquid $H_T - H_{250C} = -25.9 + 0.4314T - 7.42 \times 10^{-5}T^2$ $c_p = 0.4314 - 14.85 \times 10^{-5}T$ = 0.327 at 700°C	
101	Ice	97°-594°	Solid $H_T - H_{0C} = 0.227T + 17 \times 10^{-5}T^2$ $c_p = 0.227 + 33 \times 10^{-5}T$ = 0.326 at 300°C	CF 54-8-135
		645°	Fusion $\Delta H_f = 56$	
		655°-916°	Liquid $H_T - H_{0C} = -68.9 + 0.531T$ $c_p = 0.53$	
102	Copper	107°-466°	Solid $H_T - H_{250C} = -9.38 + 0.2817T + 3.82 \times 10^{-5}T^2$ $c_p = 0.2817 + 7.64 \times 10^{-5}T$ = 0.305 at 300°C	CF 55-8-8
		492°	Fusion $\Delta H_f = 93$	
		532°-893°	Liquid $H_T - H_{250C} = -30.85 + 0.5839T - 10.28 \times 10^{-5}T^2$ $c_p = 0.5839 - 20.56 \times 10^{-5}T$ = 0.440 at 700°C	

*See discussion page 12

TABLE 2 (Con't.)

Mixture	Calorimeter	Temperature	Enthalpy = $H_T - H$ (cal./g.) Heat Capacity = c_p (cal./g. °C) Heat of Fusion = ΔH_f (cal.g.)	Memo by: W. D. Powers G. C. Blalock
103	Copper	127°-465° 500°* 563°-882°	Solid $H_T - H_{25°C} = -5.8 + 0.234T + 4.9 \times 10^{-5}T^2$ $c_p = 0.234 + 9.7 \times 10^{-5}T$ = 0.263 at 300°C Fusion $\Delta H_f = 68$ Liquid $H_T - H_{25°C} = -88.3 + 0.657T - 19.7 \times 10^{-5}T^2$ $c_p = 0.657 - 39.3 \times 10^{-5}T$ = 0.382 at 700°C	CF 55-5-88

*560°C is the reported melting point. The major break in the enthalpy-temperature relationship is at 500°C ($\pm 10^\circ$).

TABLE 3
Heat Capacities

Mixture	Component	Mole Per cent	Average Molecular Weight	Average Number of Atoms	Ratio $\frac{\bar{M}}{\bar{N}}$	C_p Cal./g. atom °C	
			\bar{M}	\bar{N}	\bar{N}	Solid 300°	Liquid 700°C
1	NaF	76.0	75.25	2.480	30.34	6.64	9.86
	BeF ₂	12.0					
	UF ₄	12.0					
2	NaF	46.5	121.01	2.825	42.83	6.38	9.85
	KF	26.0					
	UF ₄	27.5					
3	NaF	25.0	85.82	3.050	28.14		8.86
	BeF ₂	60.0					
	UF ₄	15.0					
12	LiF	46.5	41.29	2.000	20.65	6.81	9.35
	NaF	11.5					
	KF	42.0					
14	LiF	44.5	44.85	2.033	22.06	6.84	9.64
	NaF	10.9					
	KF	43.5					
	UF ₄	1.1					
21	NaF	4.8	112.12	3.353	33.44		9.26
	KF	50.1					
	ZrF ₄	41.3					
	UF ₄	3.8					
30	NaF	50.0	110.48	3.500	31.57	6.79	8.15
	ZrF ₄	46.0					
	UF ₄	4.0					
31	NaF	50.0	104.61	3.500	29.89	5.86	8.22
	ZrF ₄	50.0					

TABLE 3 (Con't.)

Mixture	Component	Mole Per cent	Average Molecular Weight \bar{M}	Average Number of Atoms \bar{N}	Ratio $\frac{\bar{M}}{\bar{N}}$	Cal./g. atom °C	
						Solid 300°	Liquid 700°C
33	NaF	50.0	141.32	3.500	40.38	6.70	10.90
	ZrF ₄	25.0					
	UF ₄	25.0					
39	NaF	65.0	115.20	3.050	37.77	6.50	7.52
	ZrF ₄	15.0					
	UF ₄	20.0					
40	NaF	53.0	106.73	3.410	31.30	5.70	8.33
	ZrF ₄	43.0					
	UF ₄	4.0					
44	NaF	53.5	109.77	3.395	32.33	6.11	7.60
	ZrF ₄	40.0					
	UF ₄	6.5					
70	NaF	56.0	104.44	3.320	31.46	5.98	8.12
	ZrF ₄	39.0					
	UF ₄	5.0					
82	LiF	55.0	70.35	2.750	25.58	6.52	8.36
	NaF	20.0					
	ZrF ₄	21.0					
	UF ₄	4.0					
101	LiF	57.6	43.63	2.120	20.58	6.71	10.93
	NaF	38.4					
	UF ₄	4.0					
102	LiF	50.0	42.02	2.000	21.01	6.41	9.24
	KF	50.0					
103	LiF	48.0	52.90	2.120	24.95	6.56	9.53
	KF	48.0					
	UF ₄	4.0					

TABLE 4
Enthalpies of Zirconium Base Mixtures

Mixtures	No. 30	No. 31	No. 40	No. 44	No. 70	Equations (1) (2)	No. 82	No. 21	No. 33	No. 39
Composition (Mole Percent)										
LiF							55.0			
NaF	50.0	50.0	53.0	53.5	56.0		20.0	4.8	50.0	65.0
KF								50.1		
ZrF ₄	46.0	50.0	43.0	40.0	39.0		21.0	41.3	25.0	15.0
UF ₄	4.0		4.0	6.5	5.0		4.0	3.8	25.0	20.0
Temperature										
Enthalpy (cal./g. atom) = $H_T - H_{25^\circ C}$										
Solid										
100		410	430		430	420	360			380
200		970	1000		980	980	980			1030
300		1550	1570	1550	1570	1560	1620		1190	1680
400	2150	2150	2140	2160	2180	2150	2870*	*	1860	2330
500	2830	2760	2710	2770	2830	2760	4140*		2530	2980
600									3200	3620
Liquid										
500								3940*		
600	5430	5420	5460	5520	5420	5450	5270	4860		
700	6250	6260	6290	6280	6250	6270	6130	5790	5950	5940
800	7060	7060	7120	7040	7050	7070	6950	6720	7040	6690
900	7830	7840	7950	7800	7830	7850	7730	7640	8130	7440
Heat of Fusion (cal./g. atom)										
	1780	1820	1970	2040	1790		*	*	1700	1570

*See discussion page 12

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TABLE 5
Enthalpies of Alkali Fluoride Base Mixtures

Mixture	No. 2	No. 12	No. 14	No. 101	No. 102	No. 103	No. 1	No. 3	Equations (3) (4)
Composition (Mole Percent)									
LiF		46.5	44.5	57.6	50.0	48.0			
NaF	46.5	11.5	10.9	38.4			76.0	25.0	
KF	26.0	42.0	43.5		50.0	48.0			
BeF ₂							12.0	60.0	
UF ₄	27.5		1.1	4.0		4.0	12.0	15.0	
Temperature									
Enthalpy $H_T - H_{25^\circ C}$ (cal./g. atom)									
Solid									
100°C		400	360	380	400	450			340
200		1010	1040	950	1020	1070			1010
300	1730	1670	1730	1590	1650	1720	1680	1330	1690
400	2370	2370	2410	2290	2300	2390	2350	2220	2360
500	3010			3070		3080			3040
600				3910				glass	3720
Liquid									
500		5160	5170		4950		3720	3100	3120*
600	5180	6090	6140		5940	5860	4700	3990	4070*
700	6160	7020	7100	6110	6880	6860	5690	4870	5020*
800	7150	7960	8070	7200	7780	7760	6670	5760	5970*
900	8130	8890	9030	8290	8640	8570	7660	6650	6910*
Heat of Fusion (cal./g. atom)									
	1290	1970	1940	1160	1960	1690	640	glass	

*The heat of fusion is to be added to these values.

TABLE 6
Experimental Enthalpies - Mixture No. 70

Capsule	Temperature °C	Enthalpy $H_T - H_{35^\circ\text{C}}$, cal./g.		Enthalpy Difference
		Observed	Calculated	
Z 102	137	18.0	18.6	-0.6
Z 101	137	18.0	18.6	-0.6
Z 101	137	18.3	18.6	-0.3
Z 101	211	32.2	31.7	0.5
Z 102	211	33.2	31.7	1.5
Z 101	211	33.6	31.7	1.9
Z 101	234	35.4	35.9	-.5
Z 101	237	35.4	36.5	-1.1
Z 102	237	36.2	36.5	-0.3
Z 101	254	39.4	39.6	-0.2
Z 102	254	40.3	39.6	0.7
Z 102	304	49.3	49.0	0.3
Z 101	308	48.4	49.8	-1.4
Z 102	358	58.8	59.5	-0.7
Z 101	358	59.4	59.5	-0.1
Z 101	360	60.4	59.9	0.5
Z 102	393	66.3	66.4	-0.1
Z 101	393	66.4	66.4	0.0
Z 101	450	77.7	78.0	-0.3
Z 101	502	88.8	88.8	0.0
Z 102	502	88.8	88.8	0.0
Z 101	503	89.6	89.0	0.6
Z 102	528	112.4*		
Z 101	531	125.7*		
Z 102	555	156.0*		
Z 101	555	157.4*		
Z 101	559	158.4*		
Z 102	567	162.0	162.1	-0.1
Z 101	567	162.2	162.1	0.1
Z 101	589	167.5	168.0	-0.5
Z 101	589	167.8	168.0	-0.2
Z 102	590	167.9	168.2	-0.3
Z 102	592	168.6	168.8	-0.2
Z 101	594	169.6	169.3	0.3
Z 101	643	183.4	182.2	1.2
Z 102	646	184.0	183.0	1.0
Z 102	690	194.1	194.4	-0.3
Z 101	692	195.1	194.9	0.2
Z 101	695	194.6	195.7	-1.1
Z 101	747	208.2	209.0	-0.8

TABLE 6 (Con't.)

Capsule	Temperature °C	Enthalpy $H_T - H_{35^{\circ}\text{C}}$, cal./g.		Enthalpy Difference
		Observed	Calculated	
Z 102	747	208.4	209.0	-0.6
Z 101	747	209.7	209.0	0.7
Z 101	797	222.0	221.7	0.3
Z 101	798	222.3	222.0	0.3
Z 102	798	221.6	222.0	-0.4
Z 101	849	234.8	234.7	0.1
Z 101	850	234.8	235.0	-0.2
Z 102	850	235.8	235.0	0.8
Z 102	886	244.2	243.8	0.4
Z 101	888	245.0	244.3	0.7
Z 102	890	243.2	244.8	-1.6
Z 101	892	245.6	245.3	0.3

*These values not used in least squares analysis.