AD 78286

Armed Services Technical Information Agency

CONFIDENTIAL

TECHNICAL REPORT 2224

FC

ICE CALORIMETER DETERMINATION OF ENTHALPY AND SPECIFIC HEAT OF ELEVEN ORGANOMETALLIC COMPOUNDS (C)

CHARLES LENCHITZ

NOVEMBER 1955

SAMUEL FELTMAN AMMUNITION LABORATORIES
PICATINNY ARSENAL
DOVER, N. J.

ORDNANCE PROJECT TA1-5002
DEPT. OF THE ARMY PROJECT 5A04-01-011

COPY 25

CONFIDENTIAL

REGRADING DATA CANNOT BE PREDETERMINED

55AA 60216 DEC 19 1955

24420

ICE CALORIMETER DETERMINATION OF ENTHALPY AND SPECIFIC HEAT OF ELEVEN ORGANOMETALLIC COMPOUNDS (C)

by

Charles Lenchitz

November 1955

Picatinny Arsenal
Dover, N. J.

Technical Report 2224

Ordnance Project TA3-5002

Dept of the Army Project 5A04-01-011

Approved:
Robert Frye
for I. O. DREWRY
Col, Ord Corps
Director,
Samuel Feltman
Ammunition Laboratories

55AA 60216

DEC 19 1955

TABLE OF CONTENTS

Tables and Figures

OBJECT

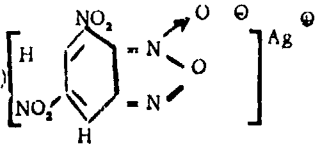
To develop a method for determining the enthalpy and the specific heat of explosives and related compounds, and to determine the enthalpy and heat capacity of eleven metal-organic and other compounds of interest in the field of explosives.

SUMMARY

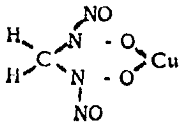
An ice calorimeter is described which can be used to determine the specific heat and enthalpy or heat content of explosives, propellants, and other sensitive compounds. The specific heat and enthalpy of the eleven compounds shown below were determined. Except for silver thiocyanate and silver cyanamide, measurements were made in the temperature range -78° to +70°C. The enthalpy of silver thiocyanate was determined between 0°C and 70°C. Measurements for silver cyanamide were made in the range -78°C to +50°C. Equations for specific heat and enthalpy of each of the compounds were calculated.

Compounds studied:

Silver thiocyanate--Ag CNS
Silver cyanamide--Ag_2 CN_2
Silverdinitrobenzfuroxan--Ag DNBF ($C_6 H_2 N_4 O_6 Ag$)



Copperthiocyanate--Cu (CNS)
Coppermethylenebisnitrosohydroxylamine (sic)
  ($C H_2 N_4 O_4 Cu$)--Cu MBNHA



Potassiumdinitrobenzfuroxan KDNBF ($C_6H_2N_4O_6$ K)
Lead methylenebisnitrosohydroxylamine
  ($CH_2 N_4 O_4 Pb$)--Pb MBNHA
Leadthiocyanate--Pb $(CNS)_2$
Lead styphnate--Pb Styphnate
Lead azide--Pb N_6
Stannous methylenebisnitrosohydroxylamine
  ($CH_2 N_4 O_4 Sn$)--Sn MBNHA

INTRODUCTION

1. A survey of the literature of explosives, propellants, and related compounds shows that the data on the thermochemical and physical properties of these compounds are not complete. The enthalpy and specific heat are but two of the properties for which there is little information. In this investigation the specific heat and the enthalpy of eleven metal-organic compounds of interest in the field of explosives and propellants were determined.

2. The compounds studied in this report include lead azide (dextrinated), lead styphnate, the cupric, stannous and lead salts of methylenebisnitrosohydroxylamine, the silver and potassium salts of dinitrobenzfuroxan, silver cyanamide, and cuprous, lead, and silver thiocyanate. These compounds were furnished by the Chemical Research Section of the Samuel Feltman Ammunition Laboratories.

3. To make these determinations an ice calorimeter was constructed, like the one developed by Robe Bunsen in 1870 (Ref A) and refined by the U. S. Bureau of Standards (Ref D, E, F) so that precision measurements could be made.

4. The ice calorimeter is also suitable for making measurements on small samples, and does not require any electrical instruments for making these measurements. All these factors make this type of calorimeter suitable for use with sensitive compounds. It was decided therefore that an apparatus similar to the one used by the National Bureau of Standards be modified for use at this installation.

5. The principle of the ice calorimeter is based on the heat of fusion of ice and the difference in density between ice and water. To measure the heat content of any substance, the substance to be measured is equilibrated at the desired temperature and then dropped into the calorimeter, which consists essentially of ice surrounded by water in contact with mercury Any difference in temperature between the sample and the ice calorimeter (which is at 0°C) is reflected by a shift in equilibrium between the solid and liquid water phases. This shift results in a displacement of mercury. The amount of mercury displaced is directly proportional to the enthalpy of the sample.

6. Laboratories in this country are using the ice calorimeter only for measuring enthalpy and heat capacity above 0°C. Swietoslawski (Ref B) stated that the ice calorimeter was used to make measurements below 0°C in European laboratories. The present study indicates that measurements made with the ice calorimeter below 0°C are as precise as measurements made above 0°C.

RESULTS

7. The results of the individual experiments are listed in Table 1. The compounds studied are designated by their chemical formulae or by abbreviations. The column "Total Gms Hg" shows the amount of mercury affected in a single experiment together with the average value for the series of experiments plus the standard deviation. The values in this column include the amount of mercury displaced from the well or the inner calorimeter by the capsule as well as the sample in the capsule. The column $H_t - H_0$ indicates the change in enthalpy in cal/gm between 0°C and any given temperature. This value includes corrections for moisture in the sample as well as the correction for the effect of the capsule on the enthalpy. (The correction for the capsule and the moisture is discussed under general errors.) The last column ($H_t - H_0$ calculated) lists the enthalpy values which are calculated from the equations of Table 2. The experimental data of the enthalpy change vs temperature is plotted in Figures 1 through 4. Except for Figure 4 each of the figures represents a class of compounds.

8. Equations for enthalpy (cal/gm) were calculated from the data of Table 1 by the method of least squares. These equations are valid for the temperature range in which the measurements were made and are shown in Table 2.

9. In Table 3 a list of the equations expressing the specific heat (Cp) cal gm^{-1} deg^{-1} of the various samples is shown. These equations are obtained by differentiating the equations of Table 2 with respect to temperature at constant pressure, i.e. $C_p = \left(\frac{\partial H}{\partial t}\right)_p$.

10. Table 4 shows the specific heat (cal gm^{-1} deg^{-1}) of the compounds at several temperatures.

DISCUSSION OF RESULTS

11. Except for Ag(CNS) and Ag_2CN_2, the equations expressing the enthalpy are applicable within the temperature range -78°C to +70°C. (Enthalpy measurements on Ag(CNS) were made between 0°C and +70°C. The enthalpy of Ag_2CN_2 was determined between -78°C and +50°C.) Values obtained from these equations do not deviate by more than the determined accuracy of the experiment. The accuracy of the experiments is shown in column (7) Table 6. The differentiation of the equations in Table 2 with temperature at constant pressure results in equations which represent the specific heat. The specific heat equations reported in Table 3 are not as precise as the enthalpy equations.

12. Table 4 shows the specific heat at several temperatures in the temperature range -50°C to +50°C. Cu MBNHA has a higher specific heat at -50°C than at 0°C. The reason for this has not been investigated. It is not known whether this is due to: (1) physical or chemical changes in the sample, (2) the presence of moisture or the moisture correction, or (3 experimental errors. (The experimental errors are discussed in a subsequent paragraph).

13. Except for PbN_6, none of the compounds listed in this study has been reported previously. Clift and Federoff (Ref G) list the specific heat of PbN_6. with or without a small quantity of paraffin, as 0.09 cal gm^{-1} deg^{-1} at room temperature. The specific heat of PbN_6 (dextrinated) taken from Table 4 is 0.110 cal gm^{-1} deg^{-1} at 25°C.

14. With the exception of Pb $(CNS)_2$, PbN_6 and Pb Styphnate, all the samples were synthesized by the Chemical Research Section at Picatinny Arsenal. The analysis of the samples synthesized at this installation is shown in Table 5. These compounds were analyzed for their metal content. In Table 5 the experimental results of the analysis are compared with the theoretical values. The analysis of the samples which were not prepared at this installation met applicable military specifications (Ref H).

15. To estimate the accuracy of the ice calorimeter and the reliability of the results, the heat capacity of a standard sample of Al_2O_3 was determined. The Al_2O_3 sample, which was furnished by the U.S. Bureau of Standards, was in the form of synthetic sapphire (corundum). Additional tests were made on benzoic acid, which is used as a standard for calibrating combustion bomb calorimeters.

16. The enthalpy values obtained in this study for these two samples are compared with those obtained by Ginnings and Furukawa (Ref C) in Table 6. The difference in the comparative values in calories is shown in columns 6 and 7 of Table 6. Values for the change in enthalpy for four temperature intervals are given for Al_2O_3. Three enthalpy values are given for benzoic acid. The average difference from the values obtained by the U.S. Bureau of Standards is 0.09 cals. This result is obtained by averaging all the values shown in column 6, Table 6. The average difference shown in column 7, Table 6 is 0.9%. The maximum percentage of difference is at 30°, where the change in enthalpy is the smallest. The difference at this temperature is 2.49%. The standard deviation is shown with each series of measurements.

17. Further examination of Table 6 indicates that the difference between the results obtained in this study, using the ice calorimeter below 0°C (i.e. -78°C), and the enthalpy values of Ginnings and Furukawa (Ref C), is 1.14% (The enthalpy experiments made below 0°C, reported by Ginnings and Furukawa, were determined in an adiabatic calorimeter). This difference (1.14%) compares favorably with the average difference at all other temperatures (.9%). Additional comparison of the enthalpy values obtained at -78°C with those obtained at other temperatures can be made by examining the standard deviations in Tables 1 and 6. In Table 6 the

standard deviation of the average enthalpy value at -78°C is + .06 cals. This standard deviation is lower than all other standard deviations shown in Table 6. In Table 1 the average standard deviation for the enthalpy measurements (gms mercury) varies from .001 to .004 gms. This variation is the same for all measurements made below 0°C (at -78°C) as well as those measurements made above 0°C. The comparisons discussed above indicate that the use of the ice calorimeter need not be restricted to high temperature measurements.

18. The general errors encountered in ice calorimetry are discussed in Refs D, E, F. Some of the errors discussed are heat leak, rate of fall of capsule, differences in pressure, sample conditioning, and capsule correction. The modification of the ice calorimeter for use with explosives required that the following two additional factors be considered: the presence of moisture in the sample, and the size of the sample used. These factors as well as some of the pertinent corrections mentioned above, are discussed below.*

a. Moisture in the sample

Because of the sensitivity of some of the compounds studied in this report, all determinations were made in a capsule which was not airtight. This precautionary measure precluded experimentation on a dry sample. Corrections were therefore made for the presence of moisture. In correcting for moisture in the sample, the specific heat for moisture above 0°C is assumed to be 1.0 cal/gm. Below 0°C the moisture is treated as ice, and the specific heat correction is 0.5 cal/gm. The correction made for each compound at the conditioning temperature is shown in Table 7. No corrections were necessary at 70°C because the sample was considered completely dried at that temperature, and the amount of moisture accumulated by the sample while reaching equilibrium in the calorimeter was negligible.

b. Size of Sample

The sensitivity of the compounds also required that the size of the sample be kept to a minimum. The volume of the capsule used was 1.3 cm. This was less than 1/7 the size of a capsule used at the U.S. Bureau of Standards.

c. Heat Leak

Because the heat leak of the calorimeter varied, corrections were made by taking rating periods before and after each drop to ascertain the quantity of mercury displaced. Table 8 shows the magnitude of the heat leak in a typical series of experiments. The percentage of heat leak is obtained by dividing the amount of Hg displaced during both rating periods by the total amount of mercury displaced in an experiment.

d. Sample Conditioning

The sample was conditioned on an oil bath on which the temperature was maintained constant within ± .05°C. Although the conditioning time was usually 40 minutes or longer, it was found that the sample reached the temperature of the bath after 30 minutes.

---

* As a result of the experience gained from this study, a larger capacity calorimeter with an airtight capsule is considered safe for use with explosives and is presently in operation in this laboratory.

e. Rate of Fall

The rate of fall of the capsule was not regulated, and the slight error introduced was considered negligible. According to Reference F the magnitude of this error was .02%-.06%, when the rate of fall varied by a factor of two and four and the conditioning temperature varied between 300°C and 900°C.

f. Condensation of Water Vapor

The calorimeter used in this study did not incoporate a flow of dry gas (helium) into the bottom of the calorimeter well. It is therefore possible that some condensation took place on the wall of the capsule while the capsule and sample are coming to equilibrium at 0°C. This error is minimized, however, as the error caused by this source in the calibration of the empty capsule largely cancels the error caused by condensation existing with the capsule containing the sample.

EXPERIMENTAL PROCEDURE

19. Apparatus

A schematic diagram of the apparatus used in this study is shown in Figure 5. Figures 6 and 7 are photographs of the apparatus presently used at Picatinny Arsenal. This latter apparatus is similar to the one which was used in this study except that its capacity is larger and it includes a flow of helium through the central well.

a. Constant Temperature Bath

A constant temperature oil bath was used to make determinations above 0°C. To perform experiments at -78°C the conditioning bath consisted of a dry ice-acetone mixture. The unit consisted of a stainless steel beaker with a brass tube in the center extending from the top of the beaker through the bottom. The brass tube was silver soldered where it passes through the bottom of the steel beaker and was considered as an extension of the central well. The capsule was suspended in this tube during the conditioning period.

b. Capsule

The capsule was made of aluminum. The cap of the capsule was made with an eyelet so that a nylon thread could be tied to it.

c. Calorimeter

The calorimeter proper consisted of a central well to which fins were soldered. This portion of the central well was enclosed in a cylindrical glass vessel. This enclosure was placed in a vacuum flask and made watertight. A glass tube extended from the bottom of the inner glass vessel to a mercury well, and thence to a weighed beaker of mercury.

Preparation of Calorimeter

20. To prepare the calorimeter, the glass vessel was completely filled with deaerated distilled water. A copper tube was then filled with dry ice and inserted into the central well of the calorimeter. This caused an ice mantle to form around the central well and the fins which were attached to the central well. The formation of ice forced water out of the calorimeter. The ice mantle was melted, and mercury was drawn into the calorimeter to compensate for the decrease in volume of the contents of the calorimeter. This procedure was repeated to insure that an adequate amount of mercury was at the bottom of the calorimeter. The final ice mantle was then formed and the calorimeter placed in an ice bath. The inner glass vessel of the ice calorimeter now contained an ice mantle surrounded by water with about twenty cc of mercury at the bottom of the glass vessel. The mercury at the bottom of the calorimeter formed a continuous column extending up through the glass tubing into the mercury well.

Determination of Enthalpy

21. The sample was placed in a cylindrical aluminum capsule which was then suspended in the well of the conditioning unit and kept there for about forty minutes. After this period the temperature of the sample and capsule had attained equilibrium (the temperature of the conditioning unit). The capsule filled with the sample was then dropped into the ice calorimeter. If the sample had been conditioned above 0°C the ice-water equilibrium within the calorimeter would shift and part of the ice mantle would melt, causing a decrease in the volume of the system and allowing mercury to be sucked into the calorimeter from the weighed beaker of mercury. If the sample had been conditioned below 0°C and dropped into the calorimeter, more ice would form on the ice mantle and mercury would be forced from the calorimeter into the weighed beaker. (The amount of mercury displaced or absorbed by the calorimeter is directly proportional to the enthalpy of the sample and the capsule). The empty capsule was then dropped into the calorimeter, and the amount of mercury displaced was subtracted from the amount of mercury affected by the capsule filled with the sample.

Determination of Calorimeter Constant

22. The calorimeter constant is based on the difference in volume between one gram of ice and one gram of water at 0°C. This change in volume caused by freezing or thawing is accompanied by the evolution or absorption of a fixed quantity of heat, the heat of fusion or heat of melting. The calorimeter constant is obtained from the equation $K = \frac{H_{fusion}}{d_m (V_{ice} - V_{water})}$, where K is the calorimeter constant in cals/gm(mercury), H_{fusion} is the heat of fusion of ice at 0°C, d_m is the density of mercury, and V_{ice}, V_{water} are the specific volumes of ice and water respectively. The numerical values used were:

$H_{fusion} = 79.7118$ cals/gm

$d_m = 13.5955$ gm/cc

$V_{ice} = 1.090857$ cc gm

$V_{water} = 1.000132$ cc/gm

When the values shown are substituted in the equation for K, the calorimeter constant K = 64.6413 cal/gm mercury. The numerical values shown above were obtained from those given in Reference D.

23. The amount of moisture in a sample at a given temperature was estimated by conditioning the sample in an oven at the same temperature. The moisture in the sample was also checked by weighing the capsule and sample at several intervals during an experiment.

REFERENCES

A. R. Bunsen, Pogg Ann 141, 1 (1870)

B. Swietoslawski, W., *Microcalorimetry* Reinhold Publishing Corp, N. Y. 1946

C. D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, 75, 522 (1953).

D. D. C. Ginnings and R. J. Corruccin, *J. Research Natl. Bur. Standards* 38, 583, Rp 1796

E. D. C. Ginnings and R. J. Corruccin, *J. Research Natl. Bur. Standards* Volume 38, 1947, R. P. 1797.

F. D. C. Ginnings, T. B. Douglas and A. F. Ball, *J Research Natl. Bur. Standards* Vol 45, 1950, RP 2110

G. G. D. Clift and B. T. Federoff, *A Manual for Explosives Laboratories,* Vol II, Lefax Co, 1943.

H. Lead Azide MIL-L-3055
Lead Thiocyanate JAN-L-65
Lead Styphnate JAN-L-757

TABLE 1

Enthalpy Values of Individual Experiments

	Temp, °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
KDNBF	-78.39 ± .01	.828		
		.836		
		.838		
		.840		
		.827		
		.834 ± .002	-16.32	-16.38
	31.16 ± .01	.327		
		.334		
		.331		
		.319		
		.324		
		.323		
		.318		
		.325		
		.318		
		.324 ± .002	7.45	7.37
	50.06 ± .01	.517		
		.521		
		.524		
		.521 ± .002	11.45	11.47
	70.06 ± .01	.738		
		.734		
		.736		
		.736 ± .001	15.68	15.80
Sn MBNHA	-78.45 ± .02	.809		
		.808		
		.803		
		.800		
		.805 ± .003	-10.95	-10.93
	31.20 ± 00	.352		
		.347		
		.352		
		.354		
		.354		
		.354		
		.354		
		.353 ± .001	4.55	4.57
	50.03 ± 00	.569		
		.573		
		.570		
		.571 ± .001	7.52	7.47
	70.46 ± .01	.807		
		.802		
		.805		
		.805 ± .001	10.82	10.82

TABLE 1 (Continued)

	Temp, °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
Cu MBNHA	-78.10 ± .06	.823		
		.827		
		.815		
		.817		
		.826		
		.822 ± .002	-14.74	-14.77
	31.20 ± .01	.354		
		.357		
		.358		
		.356 ± .001	6.13	6.06
	49.93 ± .01	.572		
		.572		
		.568		
		.571 ± .001	10.13	10.26
	70.25 ± 00	.823		
		.827		
		.815		
		.817		
		.826		
		.822 ± .002	15.54	15.50
Cu CNS	-77.97 ± .06	.992		
		1.020		
		.999		
		.996		
		1.018		
		1.008		
		1.006		
		1.023		
		.997		
		.990		
		.989		
		.985		
		1.002 ± .004	-11.76	-11.77
	31.17 ± 00	.428		
		.420		
		.430		
		.433		
		.430		
		.428 ± .002	5.1	5.19
	50.06 ± .01	.692		
		.690		
		.688		
		.693		
		.691 ± .001	8.17	8.13

TABLE 1 (Continued)

	Temp, °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
	70.35 ± .01	.967 .981 .986 .975 .976		
		.977 ± .003	11.33	11.28
Ag CNS	31.17 ± .02	.374 .367 .375 .374 .366		
		.371 ± .002	3.69	3.68
	50.07 ± .00	.602 .597 .622 .599 .624 .580 .610 .592		
		.603 ± .004	6.00	5.92
	70.36 ± .01	.849 .854 .857 .855		
		.854 ± .002	8.26	8.32
Ag DNBF	-78.25 ± 00	.811 .804 .813 .808 .809		
		.809 ± .002	-13.01	-13.08
	31.20 ± .01	.353 .354 .356 .356		
		.355 ±.001	5.44	5.86
	50.05 ± 00	.583 .584 .581 .581 .586		
		.583 ± .001	9.41	9.12
	70.41 ± .02	.816 .815 .816 .825		
		.818 ± .002	12.68	12.64

TABLE 1 (Continued)

	Temp. °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
Ag_2CN_2	-77.91 ± .00	.836		
		831		
		.849		
		.849		
		.846		
		.842 ± .004	-6.96	-6.89
	31.23 ± .01	.368		
		.371		
		.368		
		.369 ± .001	3.08	3.00
	49.94 ± .00	.587		
		.582		
		.576		
		.552*		
		.582 ± .003	4.68	4.69
Pb MBNHA	-78.05 ± .06	.818		
		.825		
		.831		
		.823		
		.830		
		.825 ± .002	-8.76	-8.77
	31.21 ± .01	.364		
		.363		
		.361		
		.361		
		.362 ± .001	3.83	3.85
	50.09 ± .003	.576		
		.576		
		.584		
		.579		
		.579 ± .002	6.01	6.01
	70.44 ± .009	.824		
		.832		
		.821		
		.823		
		.831		
		.826 ± .002	8.44	8.39

* Not included in results.

TABLE 1 (Continued)

	Temp, °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
$Pb(CNS)_2$	-78.12 ± .07	.923 .933 .929 .927		—
		.928 ± .002	-8.11	-8.09
	31.19 ± .00	.394 .391 .389		
		.391 ± .002	3.20	3.23
	50.19 ± .01	.631 .640 .633 .640		
		636 ± .002	5.24	5.20
	70.12 ± .01	.891 .894 .895		
		.893 ± .001	7.17	7.26
$Pb N_6$	-77.99 ± .10	.915 .918 .911 .920		
		.916 ± .002	-8.34	-8.42
	31.21 ± .00	.415 .401 .420 .401 .413		
		.410 ± .004	3.54	3.61
	50.04 ± 00	.648 .664 .654 .655 .634 .653 .640 .652		
		.650 ± .003	5.84	5.69
	70.38 ± .01	.898 .908 .892 .914 .904 .910 .901		
		.904 ± .003	7.83	7.88

TABLE 1 (Continued)

	Temp, °C	Total Gms, Hg	$(H_t - H_o)$ cals/gm (corr)	$H_t - H_o$ cals/gm calculated
Pb Styphnate	-78.42 ± .02	1.031		
		1.025		
		1.028		
		1.023		
		1.028		
		1.027 ± .001	-11.48	-11.44
	31.23 ± .01	.452		
		.453		
		.456		
		.454 ± .001	5.06	5.04
	49.86 ± .01	.732		
		.732		
		.729		
		.731 ± .002	8.16	8.16
	70.20 ± .00	1.045		
		1.046		
		1.048		
		1.046 ± .001	11.66	11.61

TABLE 2

Equations for Determining the Enthalpy Between -78°C and +70°C

Sample	$H_t - H_0$°C
KDNBF	$2.168 \times 10^{-1}T + .62$
Sn MBNHA	$1.426 \times 10^{-1}T + 9.783 \times 10^{-5}T^2 + 8.361 \times 10^{-7}T^3$
Cu CNS	$1.554 \times 10^{-1}T + .35$
Cu MBNHA	$1.826 \times 10^{-1}T + 2.409 \times 10^{-4}T^2 + 4.318 \times 10^{-6}T^3$
Ag DNBF	$1.73 \times 10^{-1}T + .46$
Ag_2 CN_2*	$9.05 \times 10^{-2}T + .17$
Pb MBNHA	$1.156 \times 10^{-1}T + .25$
Pb $(CNS)_2$	$1.036 \times 10^{-1}T$
Pb N_6(dextrinated)	$1.098 \times 10^{-1}T + .19$
Pb Styphnate	$1.579 \times 10^{-1}T + 1.270 \times 10^{-4}T^2 - 2.558 \times 10^{-7}T^3$
Ag CNS**	$1.183 \times 10^{-1}T$

* Equation applicable from -78°C to +50°C

** Equation applicable from 0°C to 70°C

TABLE 3

Specific Heat Equations (cal gm^{-1} $deg^{-1}C°$) from -78°C to +70°C

	$C_p \left(\frac{\partial H}{\partial T} \right)_p$
KDNBF	2.158×10^{-1}
Sn MBNHA	$1.426 \times 10^{-1} + 1.957 \times 10^{-4}t + 0.251 \times 10^{-6}t^2$
Cu CNS	1.554×10^{-1}
Cu MBNHA	$1.826 \times 10^{-1} + 4.818 \times 10^{-4}T + 1.295 \times 10^{-6}T^2$
Ag CNS*	1.183×10^{-1}
Ag DNBF	1.73×10^{-1}
Ag_2CN_2*	9.05×10^{-2}
Pb MBNHA	1.156×10^{-1}
Pb $(CNS)_2$	1.036×10^{-1}
Pb N_6(dextrinated)	1.098×10^{-1}
Pb Styphnate	$1.579 \times 10^{-1} + 2.540 \times 10^{-4}T - 0.077 \times 10^{-6}T^2$

* See footnotes in Table 2.

TABLE 4

Specific Heat cal gm^{-1} deg^{-1}C

Compound	-50°C	0°C	25°C	50°C
KDNBF	0.217	0.217	0.217	0.217
Sn MBNHA	0.139	0.143	0.149	0.159
Cu CNS	0.155	0.155	0.155	0.155
Cu MBNHA	0.191	0.183	0.203	0.239
Ag CNS	---	0.118	0.118	0.118
Ag DNBF	0.173	0.173	0.173	0.173
Ag_2CN_2	0.0905	0.0905	0.0905	---
Pb MBNHA	0.116	0.116	0.116	0.116
Pb $(CNS)_2$	0.104	0.104	0.104	0.104
Pb Styphnate	0.141	0.158	0.164	0.167
Pb N_6	0.110	0.110	0.110	0.110

TABLE 5

Metal Content of Compounds

Compound	% Metal (Experimental)	% Metal (Theoretical)
Sn MBNHA	46.87	46.96
Cu MBNHA	31.90	32.16
Pb MBNHA	60.67	60.72
Ag DNBF	31.87	32.20
K DNBF	14.83	14.74
Cu (CNS)	51.80	52.24
Ag_2CN_2	84.30	84.35
Ag CNS	64.50	65.00

TABLE 6

Comparison of Enthalpy Values (cal/gm) of Aluminum Oxide and Benzoic Acid Obtained by Experiment With Those Derived by the National Bureau of Standards

Temp °C (1)	$H_t - H_o$ cal/capsule (2)	$H_t - H_o$ Cap + 2.9606 gm Al_2O_3 (3)	$H_t - H_o$ cal/gm (corrected) Al_2O_3 (4)	$H_t - H_o$ cal/gm Al_2O_3 (NBS) (5)	Difference (cals) (6)	Difference % (7)
-78.09°C	38.45	71.99				
± .02	38.38	71.88				
	37.59	72.10				
	37.65	72.10				
	38.25	71.84				
	37.79	72.25				
	37.86	72.27				
	38.18	72.10				
	37.97					
	38.12					
	38.02 ± .09	72.07 ± .06	-11.49	-11.36	+ .13	1.14%
31.21 ±	16.57	33.07				
.01	16.73	33.41				
	16.41	32.80				
	16.82	33.44				
	16.48	32.52				
	16.58 ± .08	32.99				
		32.96				
		33.03 ± .12	5.48	5.62	- .14	2.49%

TABLE 6 (Continued)

Temp °C (1)	$H_t - H_o$ cal/capsule (2)	$H_t - H_o$ Cap + 2.9606 gm Al_2O_3 (3)	$H_t - H_c$ cal/gm (corrected) Al_2O_3 (4)	$H_t - H_o$ cal/gm Al_2O_3 (NBS) (5)	Difference (cals) (6)	Difference % (7)
50.12 ± .01	27.06	55.39				
	27.16	55.51				
	26.91	55.39				
	27.08	55.20				
	27.22	55.64				
	27.18	55.44				
	27.10 ± .05	54.76				
		54.94				
		55.28 ± .11	9.24	9.27	-.03	.32%
70.24°C ± .00	37.93					
	37.84					
	37.15					
	38.74					
	37.05					
	37.90					
	38.05	77.80				
	38.13	77.68				
	38.53	77.43				
	38.58	77.36				
	38.75	76.96				
	38.73	77.38				
	38.57	77.32				
	38.12 ± .16	77.42 ± .10	13.27	13.30	- .03	.22%

TABLE 6 (Continued)

Temp °C (1)	$H_t - H_o$ cal/capsule (2)	$H_t - H_o$ Cap + .9884 gm Benzoic Acid (3)	$H_t - H_o$ cal/gm (corrected) Benzoic Acid (4)	$H_t - H_o$ cal/gm NBS (5)	Difference (cals) (6)	Difference % (7)
31.14°C	16.67	24.64				
		24.67				
		26.05				
		25.33				
		25.54				
		25.38				
		25.68				
		25.33 ± .20	8.75	8.68	+ .07	.81%
50.11°C	27.06	41.67				
		40.74				
		40.83				
		41.27				
		41.06				
		41.52				
		41.12				
		41.12				
		41.17 ± .11	14.26	14.40	- .14	.97%
70.06°C	37.96	58.54				
		58.15				
		58.88				
		58.09				
		58.47				
		58.43 ± .23	20.69	20.77	- .08	.38%
			Average		.09 cals	.90%

TABLE 7

Moisture Corrections in Cals*

Compound	-78°C	31°C	50°C
KDNBF	.02	.03	.00
Sn MBNHA	.63	.51	.72
Cu CNS	1.40	.03	.00
Cu MBNHA	1.16	.42	.30
Ag CNS	--	.00	.00
Ag DNBF	.22	.13	.08
Ag_2CN_2	.90	.14	.00
Pb MBNHA	.15	.10	.00
Pb $(CNS)_2$	.08	.06	.00
Pb (N_6)	.24	.27	.22
Pb Styphnate	.07	.04	.06

* At 70°C no corrections were needed.

TABLE 8

Heat Leak During Several Al_2O_3 Experiments

Temperature, °C		% Heat Leak
-78.09		.2
		.3
		.4
		.2
		.3
		.4
		.4
		.3
	Average	.3%
31.21		.6
		.1
		.0
		.2
		.4
		.4
		.6
	Average	.3%
50.12		.7
		.4
		.6
		1.1
		.2
		.3
		-3
		.2
	Average	.5%
70.24		1.2
		1.0
		1.2
		.2
		.3
		.3
		.4
	Average	.6%

FIGURE 1

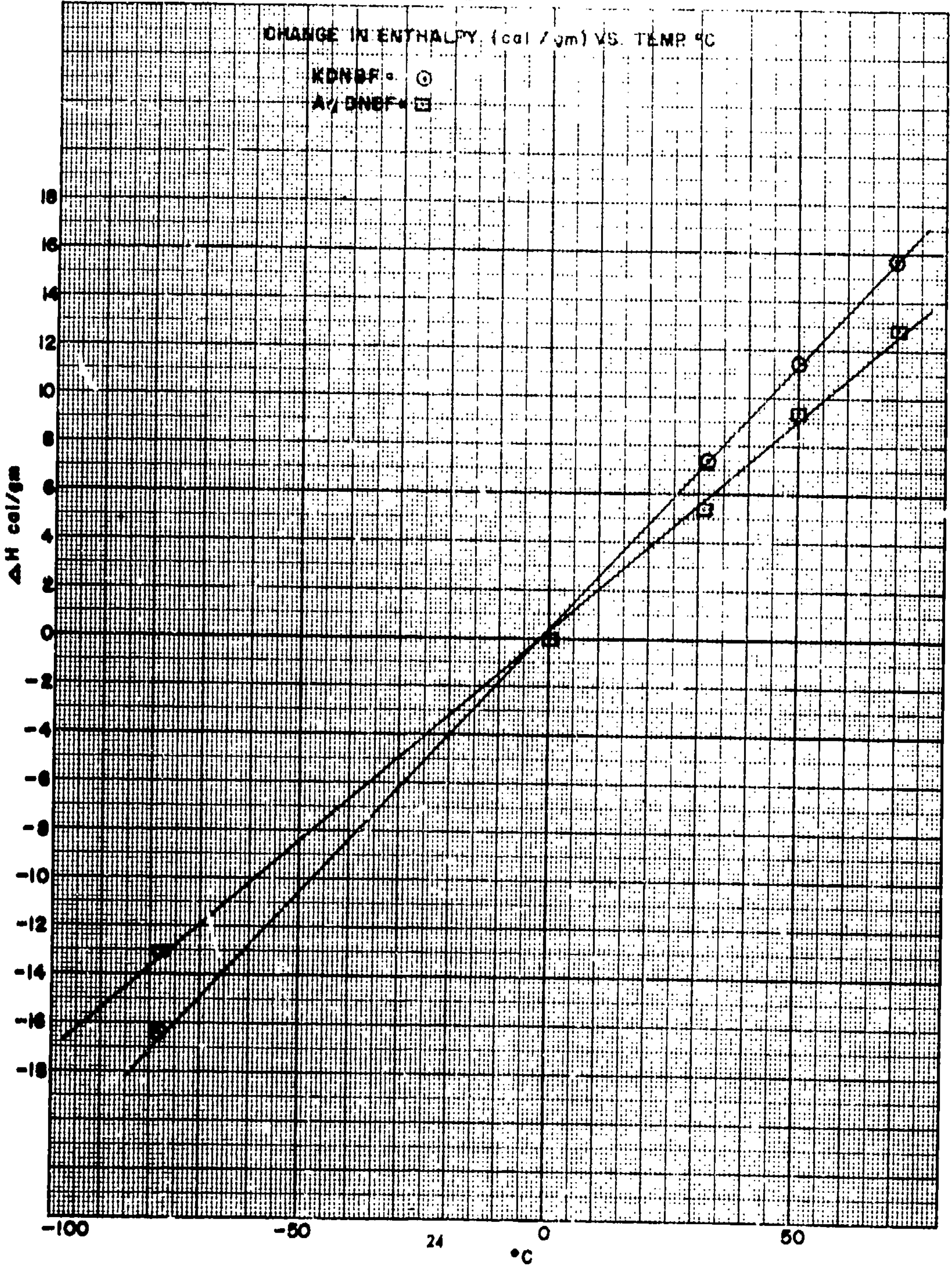

CHANGE IN ENTHALPY (cal / gm) VS. TEMP °C
KDNBF = ⊙
Al/DNBF = ⊡
ΔH cal/gm
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-100
-50
0
50
°C

FIGURE 2

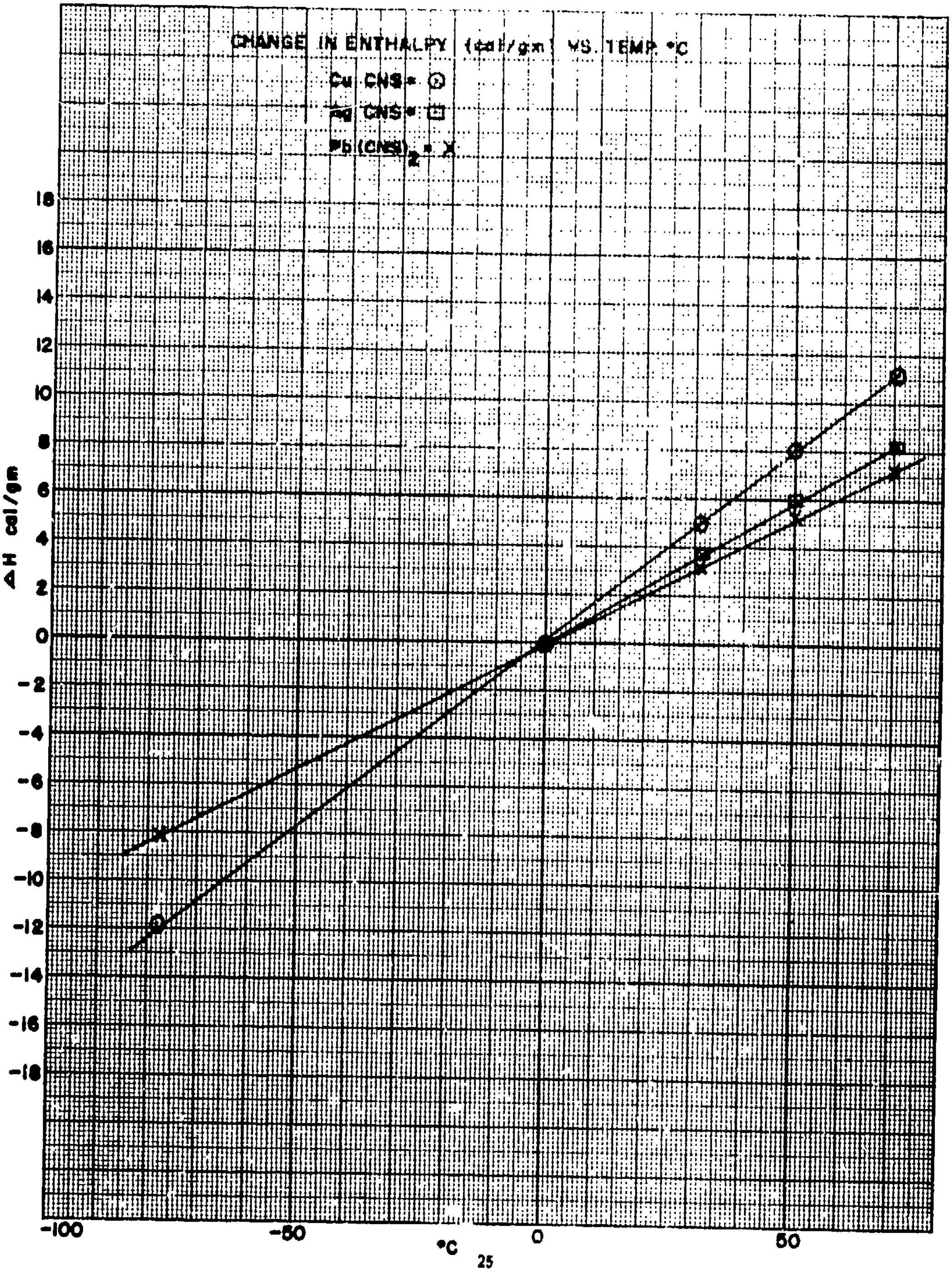

CHANGE IN ENTHALPY (cal/gm) VS. TEMP. °C
Cu CNS = ⊙
Ag CNS = □
Pb (CNS)$_2$ = X
ΔH cal/gm
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-100
-50
0
50
°C

FIGURE 3

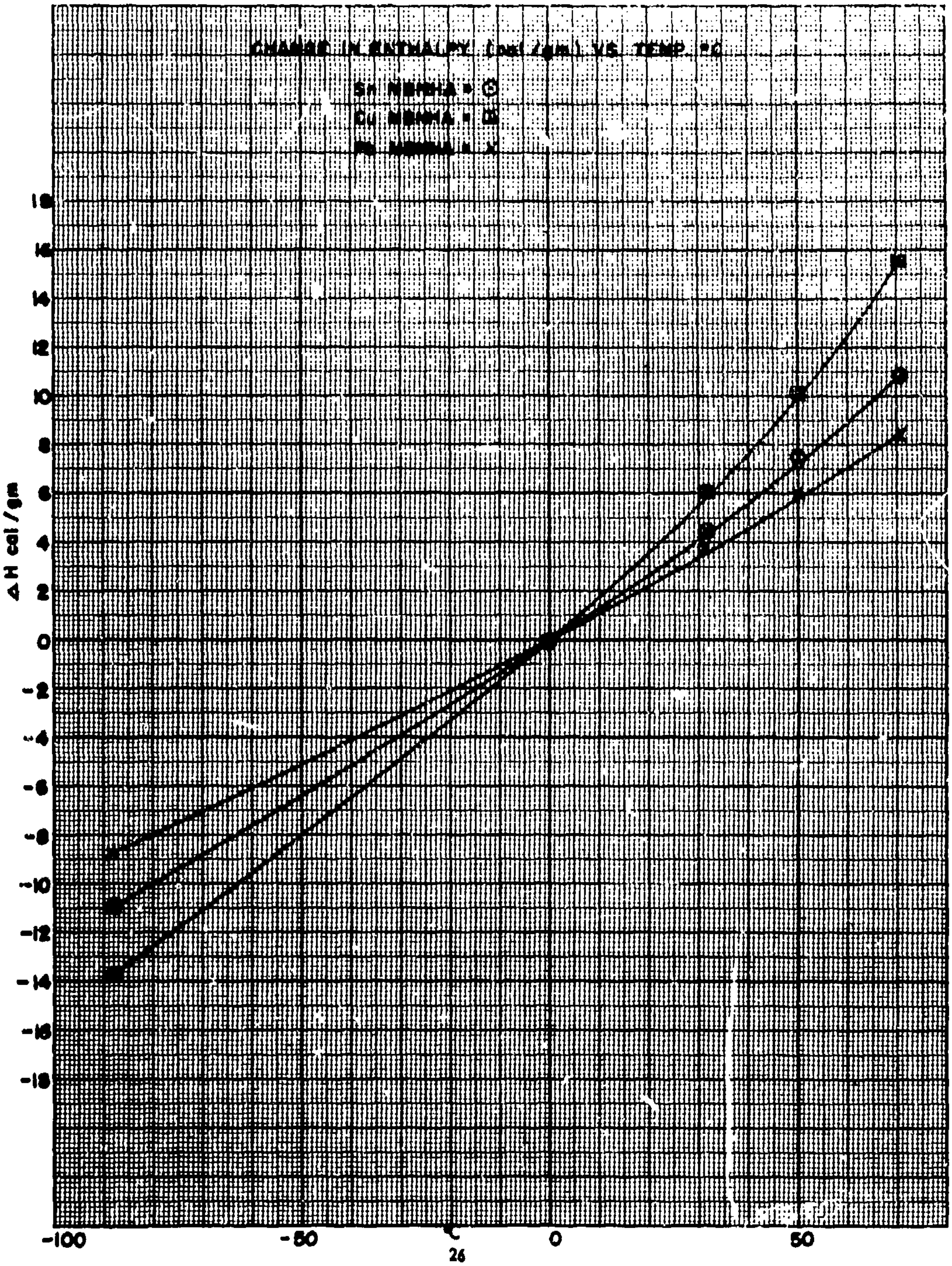
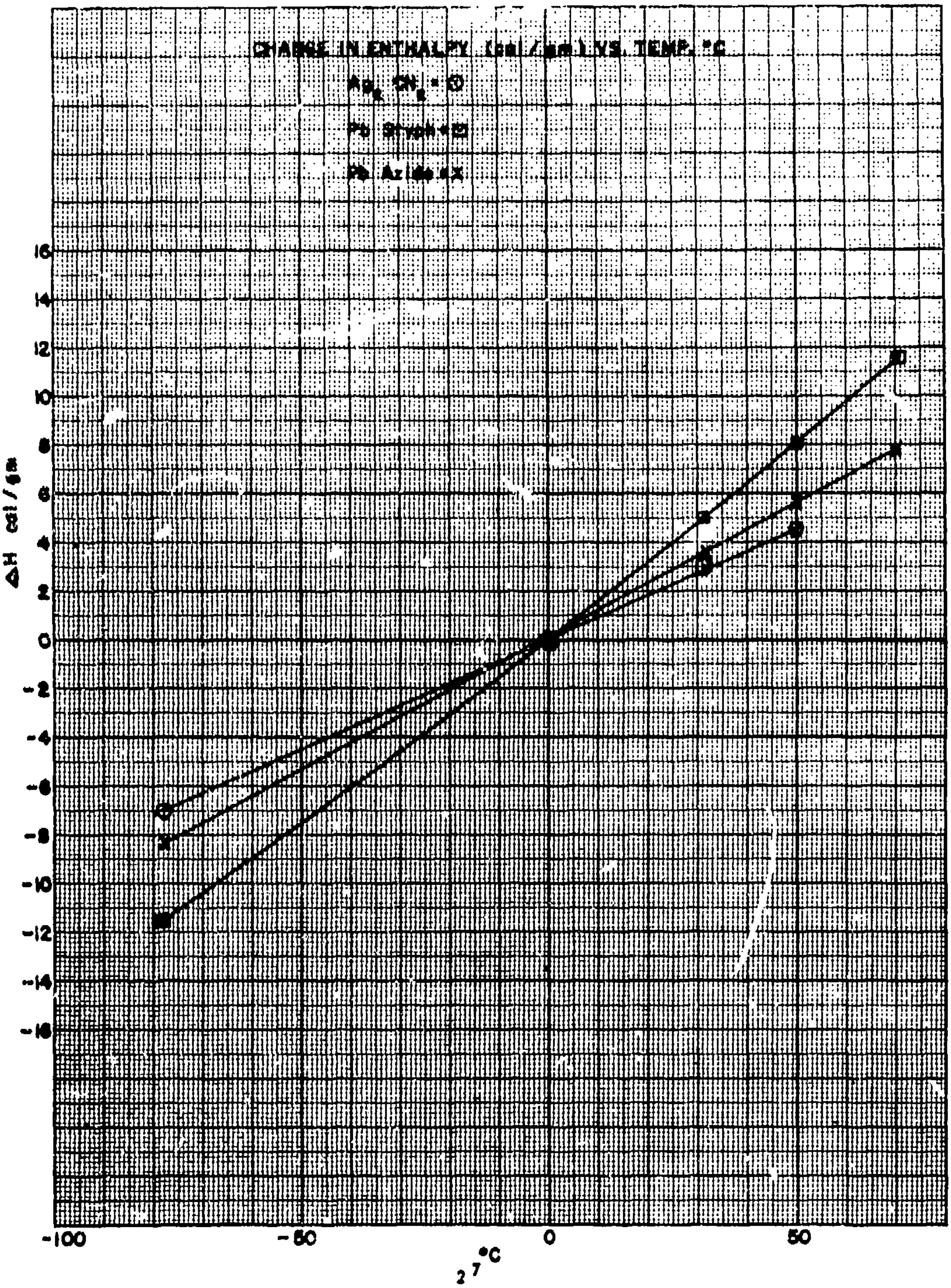
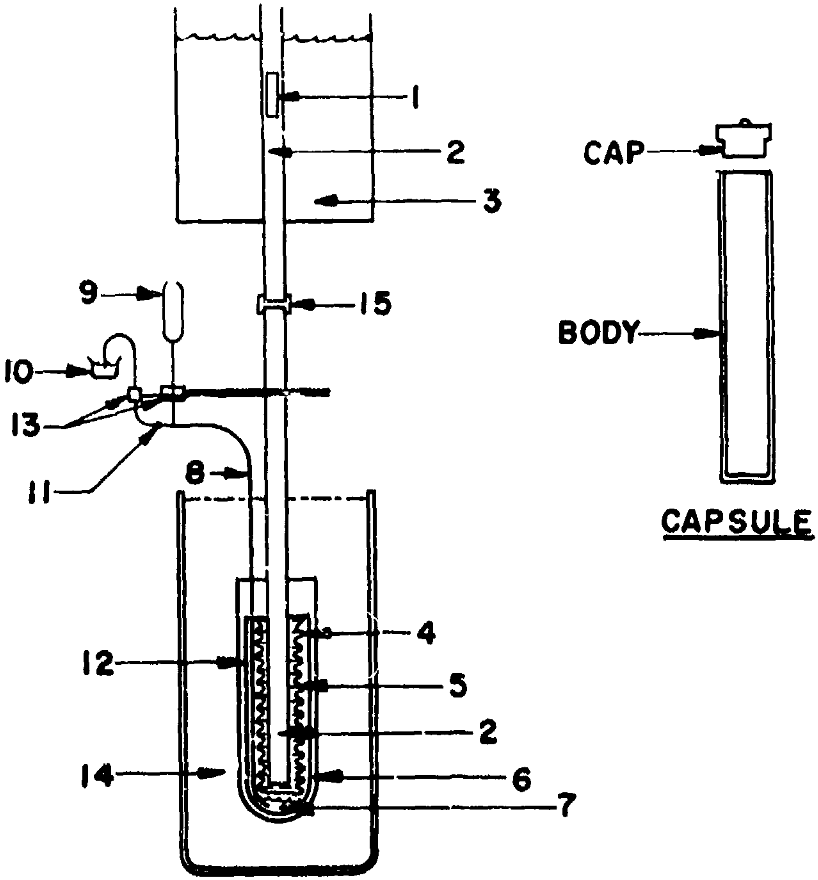

CHANGE IN ENTHALPY (cal/gm) VS TEMP °C
Sn NBIHA = ⊙
Cu NBIHA = ⊠
Pb NBIHA = X
ΔH cal/gm
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-100
-50
0
50
°C

FIGURE 4


CHANGE IN ENTHALPY (cal/gm) VS. TEMP. °C
Ag$_2$ CN$_2$ = ⊙
Pb Styph = ⊡
Pb Azide = X
ΔH cal/gm
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-100
-50
0
50
°C

ICE CALORIMETER ASSEMBLY

FIGURE 5



1 - CAPSULE
2 - CENTRAL WELL
3 - CONDITIONING BATH
4 - ICE MANTLE
5 - COPPER VANES
6 - VACUUM BOTTLE
7 - MERCURY
8 - MERCURY TUBE

9 - MERCURY WELL
10 - WEIGHED MERCURY BEAKER
11 - STOPCOCK
12 - INNER GLASS VESSEL
13 GRADUATED SCALE
14 - ICE BATH
15 - PLASTIC COUPLING

Fig 5

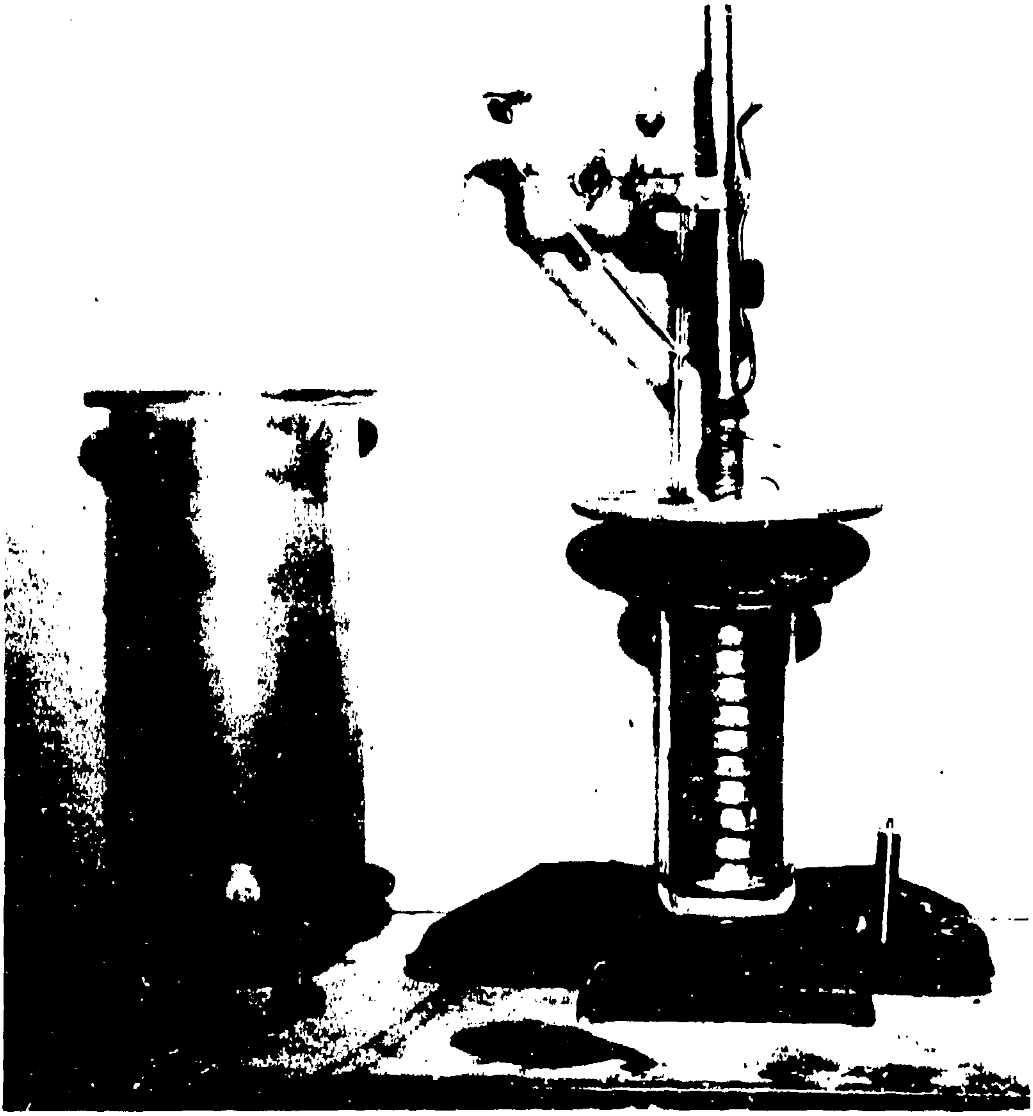


Figure 6 Ice Calorimeter, Partial Disassembly

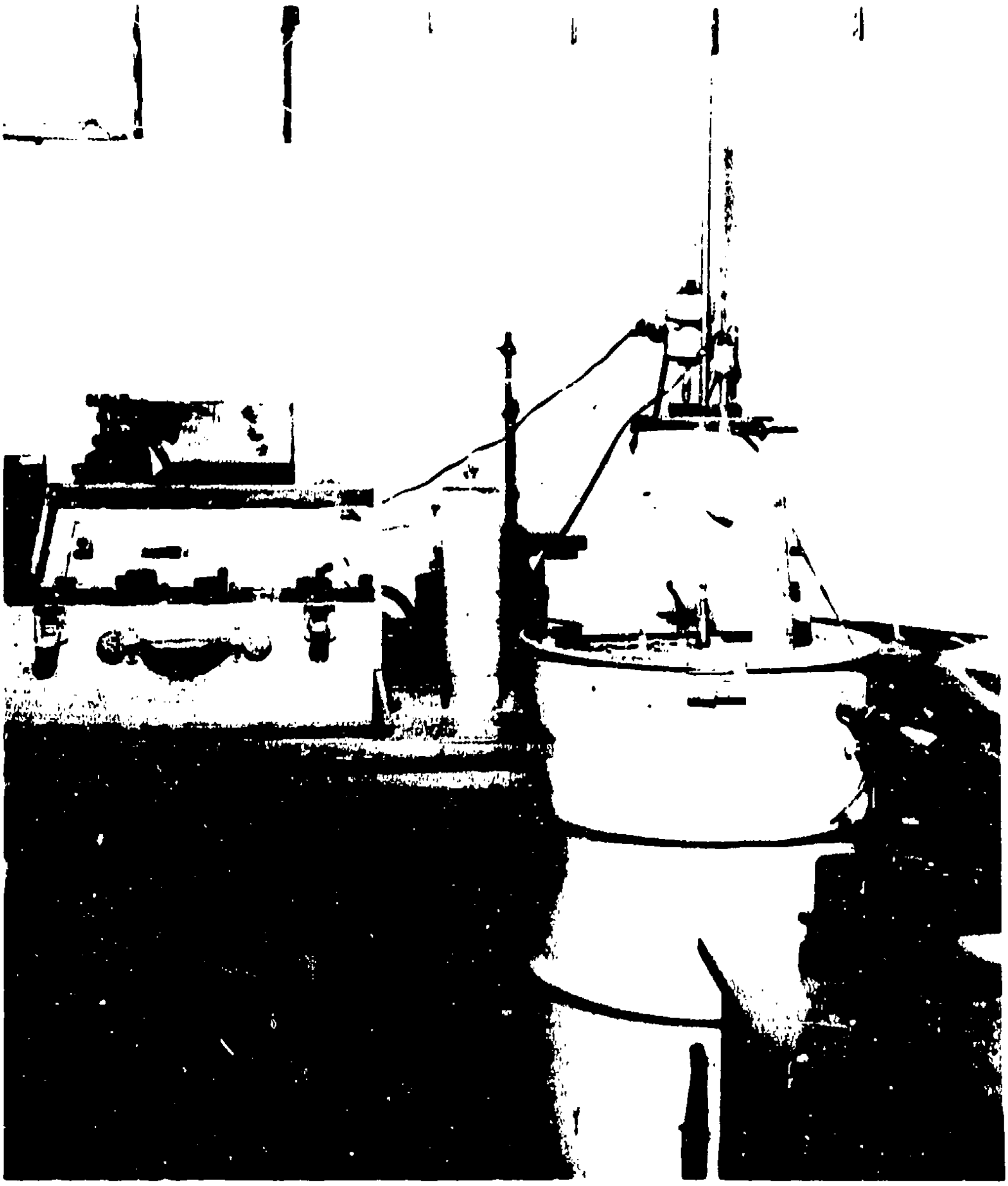


Figure 7 Ice Calorimeter with Heating and Measuring Units

DISTRIBUTION LIST

Picatinny Arsenal Technical Report 2224

	Copy No.
Commanding General Picatinny Arsenal Dover, New Jersey ATTN: Technical Information Section	1 - 5
Chief of Ordnance Dept of the Army Washington 25, D. C. ATTN: ORDTA	6
ORDTB	7
ORDTX-AR	8
Commanding General Aberdeen Proving Ground Maryland ATTN: BRL	9
Commanding Officer Technical Command Army Chemical Center Maryland	10
Bureau of Mines 4800 Forbes Street Pittsburgh, Pa.	11
Director National Bureau of Standards Washington, D. C.	12
Commanding Officer Frankford Arsenal Philadelphia, Pa	13
Commanding Officer Diamond Ordnance Fuze Laboratory Washington, D. C.	14

	Copy No.
Commanding Officer Redstone Arsenal Huntsville, Alabama ATTN: Technical Library	15
Commanding General Wright Development Center Wright-Patterson Air Force Base Ohio	16
Commanding General Ordnance Ammunition Command Joliet, Illinois ATTN: ORDLY-R	17
Commanding Officer Joliet Arsenal Joliet, Illinois	18 - 19
University of Texas Bureau of Industrial Chemistry Austin 12, Texas ATTN: Dr. K. A. Kobe Contract No. DA-23-072-ORD-(P)-6	20
U. S. Atomic Energy Commission Division of Military Application Washington 25, D. C.	21
Arthur D. Little, Inc 30 Memorial Drive Cambridge 42, Massachusetts ATTN: Dr. W. C. Lothrop Contract No. DA1-19-020-501-ORD-(P)-33	22
Commander Naval Ordnance Test Station Inyokern, China Lake California	23

	Copy No.
Commander Naval Ordnance Laboratory White Oak, Silver Spring Maryland	24
Armed Services Technical Information Agency Document Service Center Knott Building Dayton 2, Ohio ATTN: DSC-SD	25 - 34
British Joint Services Mission Technical Services 1800 K Street, N.W. Washington, D. C. ATTN: Miss Mary G. Scott	35 - 36
Canadian Joint Mission 2450 Massachusetts Ave., N.W. Washington 6, D. C. ATTN: Lt. Col. C. A. Greenleaf	37 - 38
Dept of the Navy Bureau of Ordnance Washington 25, D. C. ATTN: Ad3, Tech Library	39
Re2C	40

UNCLASSIFIED

UNCLASSIFIED