SOME THERMAL CONSTANTS OF CARBON DIOXIDE

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A Thesis

by

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Introduction

For many years, low temperature research has held a certain fascination for many workers. The results of investigation, however, have not been very plentiful, especially in the realm of latent heats of fusion. In reality there are very few substances whose latent heats of fusion and specific heats at low temperatures are accurately known. Regardless of this fact, many investigators have promulgated theories based on low temperature data that are hardly permissible because of the small number of experimental results available. It is a fundamental teaching with regard to any of the Pure Sciences that sufficient observations and classifications must be effected before an hypothesis or a theory can, with safety, be enunciated.

The present thesis is an attempt to make a slight contribution to the already existing determinations of thermal constants in the region of low temperatures.

Carbon dioxide, with which this paper deals, is but one of many important substances about which few experimental data with regard to the the thermal constants exist. Many factors make the study of this very common compound of particular interest.

In the first place, carbon dioxide is one of a small number of peculiar substances whose melting-point is higher than the boiling-point. Solid carbon dioxide at atmospheric pressure passes directly into the vapour phase without the intermediary of the usual liquid state.

Another factor that makes the study of carbon dioxide of interest, particularly in this laboratory, is the fact that its constants are peculiarly useful as aids in the determination of the New Equation of State that is at present under development here.

Then, apart from these purely philosophical considerations, compressed carbon dioxide is becoming more and more important in the industrial world. This has led to the necessity for new and better apparatus for its manufacture and, where a refrigeration method is employed, the thermal constant of carbon dioxide must be known.

The subject matter of this paper is divided into two parts for convenience in description. The first section deals with the "Determination of the Specific Heats of Carbon Dioxide over a Temperature Range from -183.1 °C to + 25°C", and the "Latent Heat of Fusion of Carbon Dioxide" ; while the second treats of the "Total Heat of Carbon Dioxide from -78.5°C to 0°C", and the "Latent Heats of Sublimation and Evaporation of Carbon Dioxide".

The theoretical significance of the results obtained in the two sections will be considered together after the experimental details comprising the two divisions have been dealt with.

It has also been considered pertinent to include an Appendix on the "Preliminary Work on the Determination of the Coefficient of Expansion of Solid Carbon Dioxide", for reasons that will be brought out in the theoretical considerations of the results obtained in the measurement of the thermal constants.

Determination of Specific Heats of Carbon Dioxide from -183.1°C to +25°C.

and

Determination of Latent Heat of Fusion of Carbon Dioxide

Method:

The method employed in the determinations of the specific heats and latent heat of fusion was briefly as follows.

A closed metal container, filled with carbon dioxide, was weighed and then allowed to come to an initial temperature in a brass tube, so arranged that heat losses were reduced to a minimum. The container and contents were then removed to an adiabatic calorimeter where the calories taken up by the carbon dioxide and its container were measured, the total heat taken up being corrected to a final temperature of +25°C.

The container was next emptied and weighed, after which a blank test was made on the container alone over the same temperature range.

From these values the specific heat per gram of carbon dioxide from a known initial temperature to + 25°C was calculated. A number of determinations were made with different initial temperatures and the total heats obtained were plotted on a curve. From this curve the latent heat of fusion of carbon dioxide was determined.

Apparatus:

The adiabatic calorimeter that was used is shown in Figure I.

The copper calorimeter vessel (D) had a capacity of 1300 c.cs., while the outer bath (K) contained 10 litres of water. The copper calorimeter was set on legs (G) that were cemented to the outer bath as shown.

Considerable attention was paid to the stirring because of the necessity for a rapid equalization of temperature throughout the bath when hot or cold water was added. Four stirrers, (not shown in figure) each with two pairs of propeller blades, were rotated in opposed directions so that each stirrer forced the water in the opposite direction to the one on each side of it. This stirring was so efficient that the addition of 100 c.cs. of water at 40°C. to the bath at 20°C, resulting in a total temperature change of 0.2°, caused temperature to be established to within 0.01°C. of the final reading, in three seconds. This shows that the temperature of the outer bath could be rapidly regulated to correspond to the changes taking place in the calorimeter vessel.

A multiple thermo-couple (T) of copper and constantan was placed in the bath and calorimeter as shown in Figure I. The usual precautions were taken to ensure the proper working of this instrument. The thermo-couple was used throughout the experiments as a null instrument.

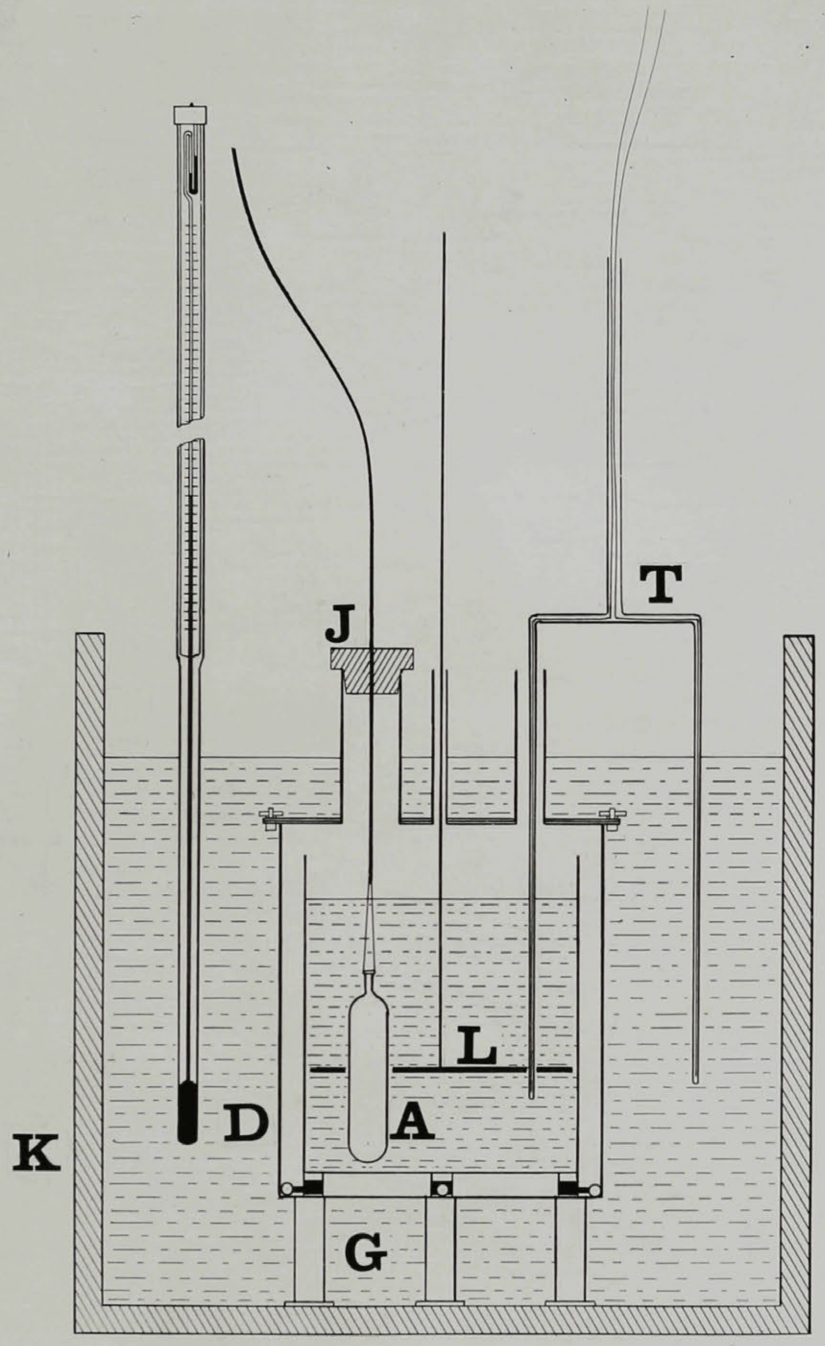


Figure I

The Adiabatic Calorimeter

D = Copper calorimeter vessel
K = Calorimeter bath
G = Legs supporting copper calorimeter vessel
J = Cork
A = Carbon dioxide container
L = Stirrer

By the addition of hot or cold water the outer bath was always kept at the same temperature as the inner calorimeter water to within 0.0005°C. Even when large temperature changes were taking place in the calorimeter, as when the cold container was suddenly introduced, it was possible to keep the temperature difference to within 0.01°C.

The temperature of the outer bath, which was exactly the same as that of the inner calorimeter, was measured by means of a Beckmann thermometer. Readings were taken to 0.001°C. This thermometer had been calibrated by the Bureau of Standards and all the precautions necessary for its use as a precision instrument were taken.

The stirring in the calorimeter was accomplished by the up-and-down motion of a copper disc (L), appropriately perforated to permit the free passage of the thermo-couple and the carbon dioxide container. The weight of the disc was sufficient to permit rapid stirring, and this was regulated by an electrically driven, adjustable eccentric.

The calorimeter vessel was insulated from its jacket by three small ivory knobs, affixed to pegs at the bottom.

The cover of the jacket was tightly clamped to a ledge at the top, which was well greased with vaseline. This made a very effective water-tight joint. A tube, wider than the carbon dioxide container, was soldered into the centre of the cover to permit of the entrance of the container to the calorimeter proper. Three other tubes of appropriate diameters served for the thermo-couple arm and for the two stirrer wires.

Constant temperature baths were used to enable the carbon dioxide to be brought to a known initial temperature before placing in the calorimeter.

For an initial temperature of 0°C. an ice-water mixture was used.

In all cases the bath liquid or mixture was placed in a Dewar flask.

For temperatures between 0°C. and -38°C. a silvered Dewar flask with an unsilvered strip down one side was employed. Ethyl ether was placed in the flask and dry air was blown through in order to effect proper stirring. The temperature was read from a mercury thermometer through the unsilvered strip in the side of the Dewar. The temperature was kept constant to within 0.1° of the required temperature by dropping small pieces of solid carbon dioxide into the ether by hand.

For temperatures from -38°C. to -78.5°C. the same arrangement was used except that the temperature was read by means of a platinum resistance thermometer. This thermometer, with compensating leads, was of the Callendar-Barnes type[1] , and was operated through a resistance box, a variable mercury resistance, and the galvanometer used in the thermo-couple circuit.

The usual solid-carbon-dioxide - ether mixture in the constant temperature bath gave an initial temperature of -78.5°C.

Temperatures between -78.5°C. and -183.1°C. were obtained with low-boiling gasoline (b.p.$<$35°C.) in the Dewar flask. The arrangement of the apparatus is shown in Figure II. Liquid air was forced into the glass cooling bulb from (A) and was allowed to cool the gasoline to the required temperature, which was then maintained constant by the addition of more liquid air from time to time. Stirring was effected, as before, by bubbling dry air from (E) through the gasoline. The platinum resistance thermometer (R) was used to determine the temperature of the bath.

The experiment at -183.1°C. was made by using liquid air alone as the liquid in the constant temperature bath.

The platinum resistance thermometer was carefully calibrated as follows.

The three fixed points chosen were those given by ice-water (0°C.), solid-carbon-dioxide - ether (-78.5°C.), and liquid air (-183.1°C.).

The liquid air was analysed for oxygen content by collecting a measured volume in a gas burette, diluting with a known amount of air and analysing the mixture for oxygen by absorption in pyrogallol in the usual manner employed in gas analysis for the determination of oxygen. From the result obtained the amount of oxygen present in the liquid air was calculated. The temperature of the liquid air corresponding to this calculated percentage of oxygen was then obtained from tables[2] and was found to be equal to -183.1°C.

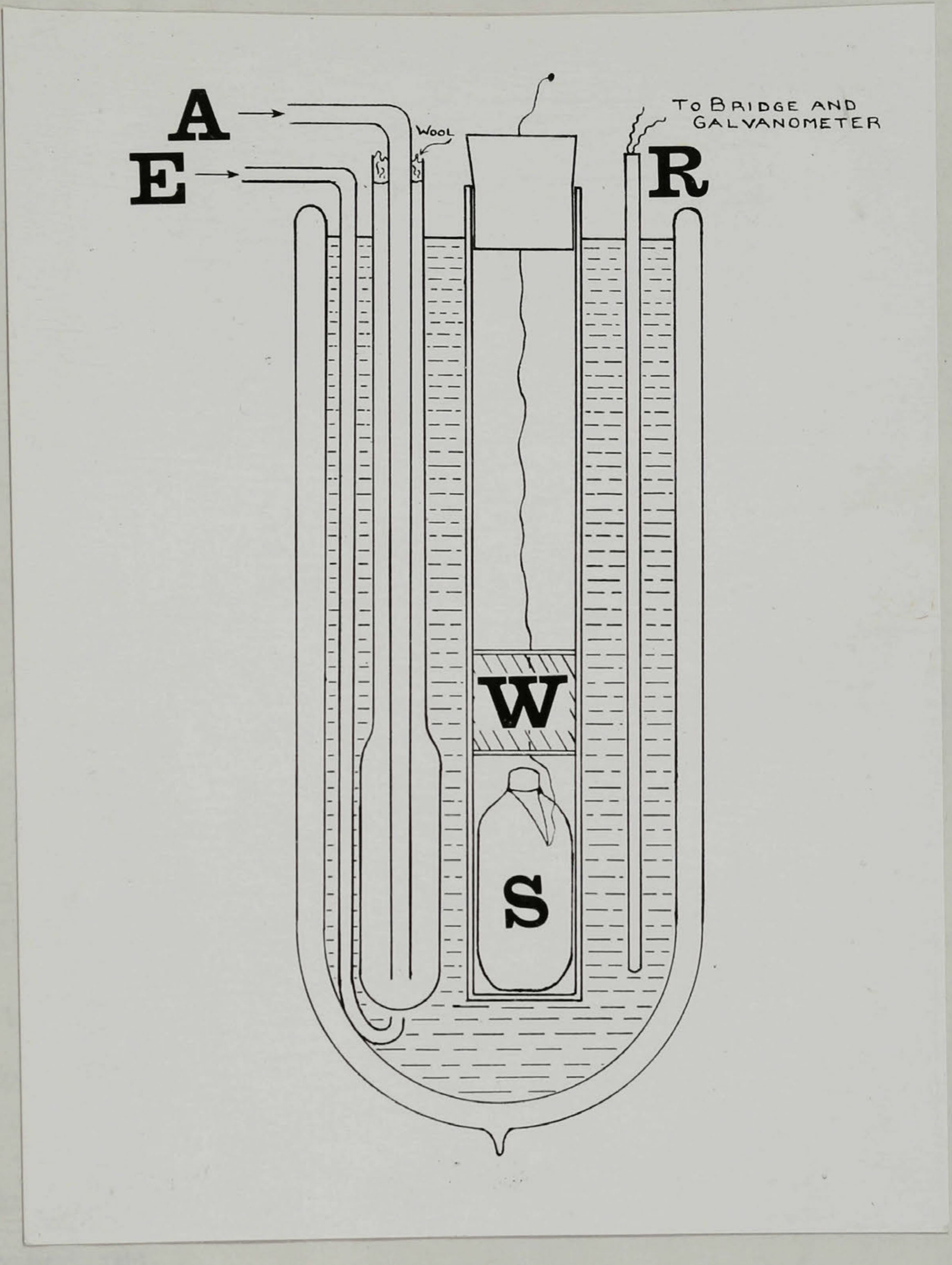


Figure II

The Constant Temperature Bath

A = Liquid air entrance
E = Dry air entrance
S = Carbon dioxide container
W = Wool plug with copper discs at top and bottom
R = Platinum resistance thermometer.

The Δ of the Callendar-Barnes formula was determined from

$$\theta_{pt} = \theta - \Delta A$$

where

$$\theta_{pt} = 100\,\frac{R - R_0}{R_{100} - R_0}$$

and

$$A = \left\{\left(\frac{\theta}{100}\right)^2 - \left(\frac{\theta}{100}\right)\right\}$$

and θ_{pt} is the temperature registered by the platinum resistance thermometer when its resistance is R.

Now by letting

$$\frac{100}{R_{100} - R_0} = \alpha$$

and knowing $R_{-78.5}$, R_0 and $R_{-183.1}$, then α was evaluated and R_{100} found.

Then, by substitution in the formula above, Δ was calculated and was found equal to 1.402.

The resistances of the thermometer were evaluated for 10° intervals and a curve was plotted to cover the range in which experiments were carried out.

The mercury thermometer was calibrated against the platinum resistance thermometer for temperatures from 0°C. to -38°C.

Procedure:

The container for the carbon dioxide was made of iron, had a capacity of 10 c.cs., and contained about 8 gms. of carbon dioxide. It was metal sealed and was strong enough to withstand the pressure due to liquid carbon dioxide up to +40°C. The container was weighed before and after each run to make certain that no loss of carbon dioxide occurred due to leakage.

This weighed container (see S in Figure II), filled with carbon dioxide, was placed in a brass tube of such a diameter that the container could just pass easily through it. One end of the tube was closed water-tight while the other was stopped with a cork. Through this cork passed a string, to which the container was attached by means of linen thread.

Two copper discs enclosing wool (see W in Figure II) served to insulate the container from the upper part of the tube.

Electric tape was wound over the side of the cork and the top of the tube. This prevented any moisture condensing on the cork or the tube and eliminated the danger of introducing water from this source into the calorimeter.

The brass tube was then suspended in the constant temperature bath and allowed to remain at a known initial temperature for a sufficient length of time to permit the carbon dioxide and container to come to this temperature, from 1 to 1½ hours being found quite satisfactory. For the points below -60°C. the brass tube and contents were kept in a solid-carbon-dioxide - ether mixture for 1 hour before placing in the constant temperature bath. This was done to prevent super-cooling of the carbon dioxide. It will be seen when thecurve obtained for the total heats is discussed that one determination at -61.3°C. did super-cool. This happened before the necessity for pre-cooling the carbon dioxide well below its melting-point was realized.

While the carbon dioxide was in the constant temperature bath the adiabatic calorimeter was prepared as follows.

The inner calorimeter vessel was weighed empty and dry. It was filled with water at a suitable temperature and re-weighed. After placing in the calorimeter jacket the cover was immediately clamped into place, the tubes in the cover for the introduction of the thermo-couple and the container being stopped with corks. The calorimeter bath was immediately filled with water to the over-flow, which allowed water to completely surround the calorimeter jacket including the cover. The thermo-couple was set in place with one arm in the calorimeter and the other in the water of the outer bath. By running in hot or cold water the temperature of the water in the outer bath was brought slightly higher than that in the calorimeter proper and maintained at this higher value until the calorimeter was required for use.

The reason for maintaining this slight difference in temperature was to prevent any distillation of the water from the calorimeter to the top and walls of the calorimeter jacket. Obviously, if the calorimeter water was colder than the outer bath, the tendency would be for water to condense into the calorimeter proper. This was rendered impossible by the closed calorimeter jacket.

Shortly before the time for the introduction into the calorimeter of the carbon dioxide and container, the water in the outer bath was brought to exactly the same temperature as the water in the calorimeter proper. From this point to the end of the experiment the two baths were kept at exactly the same temperature.

The Beckmann thermometer was read every five minutes until three successive readings did not vary more than 0.002° from one another. Conditions in the calorimeter were then known to be constant.

The electric tape was removed from the brass tube in the constant temperature bath and the carbon dioxide in its container was rapidly transferred to the calorimeter (see A in Figure I), the cork to which the container was affixed fitting the tube through which the container was introduced into the calorimeter (see J in Figure I).

Appreciable heat loss in the transference of the carbon dioxide to the calorimeter was impossible since the time required to remove the container from the constant temperature bath to the calorimeter was less than three seconds.

The insulating plug of wool and copper discs automatically fell off as the container was removed from the brass tube.

Cold water was rapidly run into the water bath surrounding the calorimeter as the water in the calorimeter proper cooled down.

When a constant temperature had again been reached, readings of the Beckmann thermometer were taken every five minutes until three successive readings agreed with one another to 0.002°.

Sample Set of Observations:

The following set of observations is given as being characteristic of those obtained throughout.

Initial temperature	-78.5° C.
Weight of calorimeter and water ...	925.00 grams
Weight of Calorimeter	269.45 "
Weight of water	655.55 "
Weight of calorimeter, stirrer and thermo-couple arm	298.2 "
Specific heat of calorimeter, stirrer and thermo-couple arm	0.0827 cals. per gr.

Beckmann thermometer readings.

Time	Beckmann
9.00 p.m.	3.543
.05	3.543
.10	3.542
.15	3.543
Introduced carbon dioxide and container	
9.20	2.100
.25	2.100
.30	2.101

Weight of container and carbon dioxide	29.5092 grams
Weight of container	21.4800 "
Weight of carbon dioxide	8.0292 "

Calculations and Results:

The following sample calculations are based on the observations given above.

Calorimeter temperature

	Initial	Final
	3.543	2.100
Correction for standard	0.0001	0.0030

Temperature change of calorimeter ... ... 1.4459°C

Setting factor for Beckmann thermometer ... 1.000

Weight of water ... ... 655.55 grams

Heat given up by calorimeter, stirrer and thermo-couple arm

$298.2 \times 0.0827 \times 1.4459 = 35.658$ calories

Heat given up by water

$655.55 \times 1.4459 = 947.863$ "

Total calorimeter heat change = 983.52 "

Heat taken up by carbon dioxide and container near +25°C. ... 6.6 cals. per degree
(from preliminary curve of Total Heats)

Final temperature of container and contents ... ... 2.10° (Beckmann)
= 23.65°C.

Total heat taken up by carbon dioxide and container from -78.5°C to +25°C ... ... 992.43 calories.

The calculation is self-explanatory and it will be seen from it how the heat change is always calculated to the same end temperature.

The values for the total heat change, given in Table I, are the means of several determinations that agreed with one another to within 0.5 per cent.

Table I

Initial temperature of Carbon Dioxide and Container	Total Heat taken up by Carbon Dioxide and Container from Initial Temperature to + 25°C.
+ 25.0 °C	0.0 calories
0.0	151.9
-37.5	396.5
-54.3	509.5
-61.4 (super-cooled)	547.8
-61.4 (solid)	908.3
-70.6	951.4
-78.5	990.3

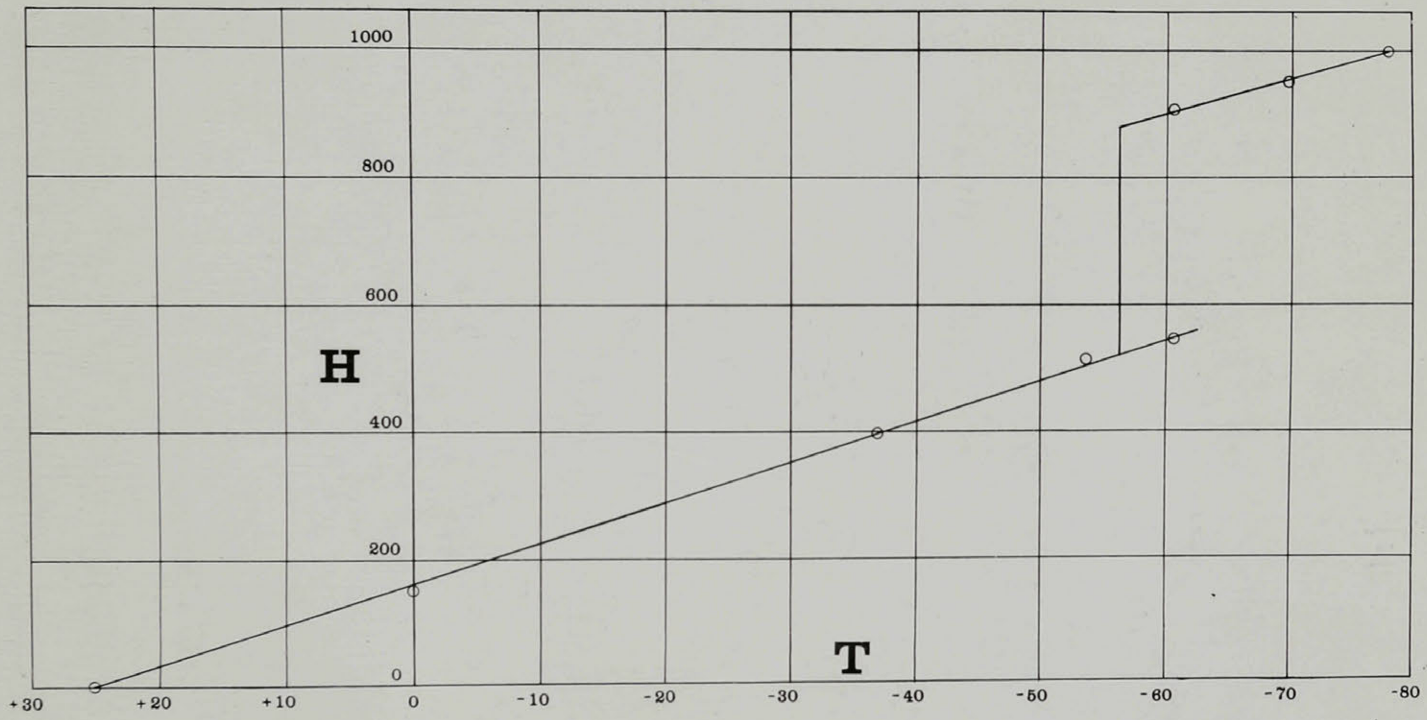
The values in Table I are plotted on Curve I. From this curve the rise in the heat taken up by the carbon dioxide at -56.2°C. (the melting-point) is equal to 364 calories.

Hence the latent heat of fusion is equal to this rise in the heat taken up divided by the weight of carbon dioxide in the container.

$$\text{Latent Heat of Fusion of Carbon Dioxide} = \frac{364}{8.029}$$

$$= 45.3 \text{ calories per grm.}$$

To obtain the specific heats of the solid and liquid carbon dioxide, the specific heat of the container was determined over the temperature range -183.1°C. to + 25°C. and a number of additional determinations of the total heats of the carbon dioxide and container were made.



Curve I

Total Heats of Carbon Dioxide and Container

from - 78.5°C to + 25°C.

T = Initial temperature of carbon dioxide and container (in degrees Centigrade)

H = Heat taken up by carbon dioxide and container from initial temperature (T) to + 25°C (in calories)

The Heat Content per Gram of Container and the Heat Content per Gram of Carbon Dioxide are given in Table II below.

Table II

Temperature °C.	Heat Content per Gram Container calories	Heat Content per Gram Carbon Dioxide calories
+25.0	0.00	0.00
0.0	2.95	11.04
-37.5	7.00	30.58
-54.3	8.20	41.90
-61.4 (super-cooled)	9.20	43.38
-61.4 (solid)	9.20	88.47
-70.6	10.02	91.70
-78.5	10.78	94.34
-115.0	13.30	104.7
-183.1	17.80	120.9

In Table II, column 1 gives the initial temperature of container and contents, columns 2 and 3 the heat required to warm up one gram of container and one gram of carbon dioxide respectively from the initial temperature to +25°C. Thus, for example, the third to last figure in column 3 (viz., 94.34) means that it requires 94.34 calories to warm up one gram of carbon dioxide from -78.5°C. (its boiling-point) to +25°C., without evaporation.

In Table III below are given the specific heats of solid carbon dioxide over three temperature ranges.

Table III

Temperature Range	Specific Heat of Solid Carbon Dioxide
-61.4°C. to -78.5°C.	0.343 cals. per gm. per degree
-78.5 " -115.0	0.284 " " "
-115.0 " -183.1	0.231 " " "

The following Table IV gives the average specific heat of the solid between the boiling-point (-78.5°C.) and the melting-point (-56.2°C.) and the average specific heat of the liquid between the melting-point (-56.2°C.) and + 25°C.

Table IV

Carbon Dioxide State	Temperature Range	Average Specific Heat
Solid	-78.5°C to -56.2°C	0.348 cal.per gm. per degree
Liquid	-56.2°C to + 25.0°C	0.490 cal.per gm. per degree

Determination of Total Heat of Carbon Dioxide from 0°C. to -78.5°C.

and

Determination of Latent Heats of Sublimation and Evaporation of Carbon Dioxide.

Method:

In the "Determination of the Total Heat of Carbon Dioxide from 0°C. to -78.5°C." a special apparatus was designed by means of which pure carbon dioxide could be generated and a known weight then condensed into a container. The container and contents did not have to be weighed at room temperature so that there was no necessity of having a container that would be able to withstand any appreciable pressure.

The solid carbon dioxide was allowed to warm up in an adiabatic calorimeter and the heat taken up by the carbon dioxide from a known initial to a known final temperature was accurately determined.

During this rise in temperature the container was open to the air so that the heat change measured was that due to the total heat of carbon dioxide without sublimation plus the latent heat of sublimation.

Apparatus:

The apparatus for the generation and condensation of the carbon dioxide is shown in Figure III. (The distillation flask O and the taps P and Q were sealed on for the determination of

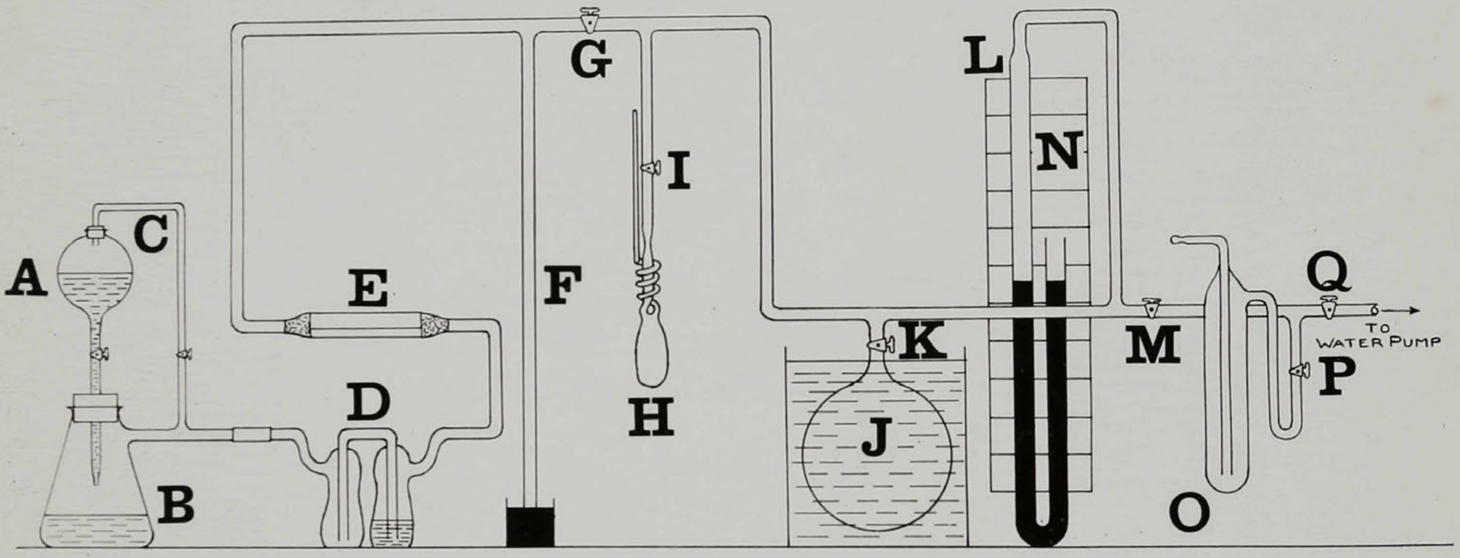


Figure III

Apparatus for Generation and Condensation of Carbon Dioxide

A = Dropping funnel
B = Flask
C = Connecting tubing
D = Sulphuric acid bubblers
E = Phosphorus pentoxide tube
F & L = Mercury manometers
H = Condensation bulb
J = Volume bulb
N = Manometer scale
O = Distillation flask
G,I,K,M,P,Q = Taps

the coefficient of expansion (see Appendix) after the experiments described in this section were completed).

Dilute sulphuric acid (1 : 6) was contained in the dropping funnel (A) and allowed to drop on a saturated solution of potassium carbonate in the flask (B).

The carbon dioxide so produced was dried by passage through the concentrated sulphuric acid bubblers (D) and then over phosphorus pentoxide in the tube (E).

By observation of the mercury manometer (F) the pressure of the carbon dioxide generated could be maintained at that of the atmosphere.

The tube (C) enabled the pressure of the gas above the sulphuric acid in (A) to be kept at the same pressure as the gas in the apparatus without the necessity of admitting air to (A).

The dried carbon dioxide was collected in the volume bulb (J), the pressure in this part of the apparatus being determinable at all times by means of the mercury manometer (L).

Condensation was effected in the glass bulb (H). The first attempt was made with a metal container fitted with a metal spiral as a receptacle for the condensed carbon dioxide, but it was found to have too high a heat conductivity. Even with the spiral surrounded by a steam coil it became so cold that carbon dioxide was condensed in it, thus blocking the passage to the container proper. Consequently the metal container was replaced by the glass bulb, which was found to be very satisfactory.

The bulb (H) was constructed to have a volume of about 20 c.cs. A glass tube at the top facilitated sealing to the main part of the carbon dioxide apparatus and could be sealed off completely after condensation of the carbon dioxide. The bulb was also fitted with a thin-walled glass spiral of small bore, through which the carbon dioxide was allowed to escape during the heat change measurements. The object of this spiral was to ensure the escaping carbon dioxide being at the same temperature as the water in the calorimeter.

This spiral was a very important feature of the glass container. The thickness of the walls was about 0.1 m.m. and the diameter of the tube was less than 2 mm. Before placing in the calorimeter the tip of this thin tube was broken and, since the other tube from the bulb was sealed off, the carbon dioxide could only escape through the spiral. In this way all the escaping carbon dioxide was enabled to come to the temperature of the water before leaving its influence.

The whole apparatus could be evacuated by means of a water pump acting through a water trap.

It was found advantageous only to evacuate that part of the apparatus to the right of tap (G), the left-hand section being maintained always at atmospheric pressure. This eliminated the danger of air leakage through the rubber connection between the flask (B) and the rest of the apparatus that might have taken place due to the higher pressure on the air side of the tubing. A rubber connection was used in order that the generator might be easily removed and cleaned out when the solution of potassium carbonate was exhausted.

Except at the flask (B) all connections were glass-blown to prevent any leakage in the apparatus.

Procedure:

The whole apparatus was swept out several times with carbon dioxide by evacuation of the part to the right of tap (G) and then by generation of carbon dioxide in the flask (B), passing through the partially opened tap (G).

After filling all the apparatus with carbon dioxide at atmospheric pressure, taps (G) and (M) were closed, care being taken to see that taps (I) and (K) were open.

A piece of tissue paper was tied around the bulb (H) and a Dewar flask filled with liquid air was carefully brought up under it.

When using the bulb (H) without the tissue paper it was found that during the condensation of the carbon dioxide, even with dry air blowing around the condensation bulb, it was impossible to prevent the deposition of a certain amount of water on the surface of the bulb. Consequently the values for the heat change, when this took place, were found to be a few calories too high and were, therefore, rejected.

Results checking to better than 0.5 per cent. were obtained by the use of the tissue paper. This paper prevented the condensation of water on the bulb and the time required to remove it before placing the bulb in the calorimeter was negligible.

As condensation in the bulb (H) took place, the left-hand column of the manometer (L) rose.

Tap (I) was then closed and the positions of the two arms of the manometer (L) were read off the scale (N).

The apparatus was refilled with carbon dioxide at atmospheric pressure by partially opening tap (G).

Tap (G) was then re-closed and, on opening tap (I), further condensation took place in the bulb (H) as shown by the rise in the left-hand column of the manometer (L).

Tap (I) was closed again and the manometer read as before.

The apparatus was filled a third time with carbon dioxide at atmospheric pressure and condensation was effected as already described.

Note was also made at the time of barometric pressure, room temperature, and the temperature of the water bath surrounding the volume bulb (J).

The glass tube connecting bulb (H) to the apparatus was sealed off completely and the bulb was immersed in liquid air for 30 minutes.

When the adiabatic calorimeter was ready, the tip of the glass spiral on the bulb (H) was broken, the tissue paper was torn off and the bulb was transferred rapidly to the calorimeter, where the heat changes occurring were carefully noted.

It was very important to have the glass spiral project above the cover of the calorimeter jacket when the bulb was in the calorimeter proper. It was found that the total heat from -183.1°C. to +25°C. was 191.5 calories (as compared with the probably correct value of 183 calories) when the carbon dioxide was allowed to escape from the bulb (H) into the space between the calorimeter proper and the calorimeter jacket. This is explained by the fact that a certain amount of water probably evaporated into the dry carbon dioxide. Even the evaporation of a small amount of the calorimeter water would have a great effect on the heat measurements because of the large latent heat of evaporation of water.

In order to calculate the amount of carbon dioxide in the bulb (H) it was necessary to know accurately the different volumes present from which it was condensed. The volume of the bulb (J) was determined, in the usual manner, by filling with water and weighing. The volumes of the tubing and of the bulb (H), respectively, were found experimentally by means of the Gas Laws.

Sample Set of Observations:

The following set of observations is characteristic of those obtained throughout this determination.

I. Apparatus filled with carbon dioxide at atmospheric pressure.

Carbon dioxide was condensed.

Reading of manometer = 69.15 - 11.75 units

II. Apparatus filled with carbon dioxide at atmospheric pressure.

Carbon dioxide was condensed.

Reading of manometer = 73.5 - 7.05 units

III Apparatus filled with carbon dioxide at atmospheric pressure.

Carbon dioxide was condensed.

Reading of manometer = 72.85 - 7.75 units

Room temperature ... ... 23°C.
Temperature of water surrounding volume bulb (J) ... ... 22°C.
Barometric pressure . ... 76.3 cms.

1 unit on manometer scale = 0.9918 cm.

Calculations and Results:

The following sample calculation is based on the observations given above.

Data:

Room temperature = T_R = 23°C. = 296° Abs.

Molecular weight of carbon dioxide at temperature T_R (from tables[3]) = M_R = 44.27 gms.

Temperature of bulb (J) = T_V = 22°C. = 295° Abs.

Molecular weight of carbon dioxide at temperature T_V (from tables[3]) = M_V = 44.27 gms.

Barometric pressure = $P_{Bar.}$ = 76.3 cms.

Volume of bulb (H) = V_B = 19.89 c.cs.

Volume of bulb (J) = V_V = 990.5 "

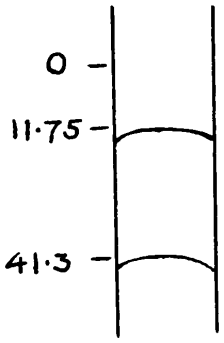
Volume of tubing = V_T = 93.4 "

Volume of manometer tubing = (length) × $\frac{5}{6.8}$

For weight of carbon dioxide condensed,

use $m = \frac{M\,P\,V}{R\,T}$

where m = weight of carbon dioxide in grams
M = molecular weight in grams
P = pressure in atmospheres
V = volume in litres
R = the gas law constant
T = absolute temperature



0 ≡ point on manometer scale to which volume of tubing (V_T) extends

11.75 ≡ upper level of mercury after condensation of carbon dioxide

41.3 ≡ level of mercury at atmospheric pressure.

Difference in levels of mercury in manometer arms

= 69.15 - 11.15 = 58.0 units

= 58.0 × 0.9918 cms.

m (from volume of manometer tubing between 0 and 11.75)

$$= \frac{M_R\,P\,V}{R\,T_R}$$

$$= \frac{44.27(58.0 \times 0.9918)\ 11.75 \times \frac{5}{6.8}}{1000 \times 0.0821 \times 296 \times 76}$$

$$= 0.01191 \text{ grams}$$

m' (from volume of manometer tubing between 41.3 and 11.75)

$$= \frac{M_R \, P_{Bar} \, V'}{R \, T_R}$$

$$= \frac{44.27 \times 76.3 \times (41.3 - 11.75) \times \frac{5}{6.8}}{1000 \times 76 \times 0.0821 \times 296}$$

$= 0.03974$ grams

m_B (from bulb (H))

$$= \frac{M_R \, P \, V_B}{R \, T_R}$$

$$= \frac{44.27 \times (58 \times 0.9918) \times 19.89}{1000 \times 76 \times 0.0821 \times 296}$$

$= 0.03453$ grams

m_T (from tubing)

$$= \frac{M_R \, P \, V_T}{R \, T_R}$$

$$= \frac{44.27 \times (58 \times 0.9918) \times 93.4}{1000 \times 76 \times 0.0821 \times 296}$$

$= 0.1288$ grams

m_V (from bulb (J))

$$= \frac{M_V \, P \, V_V}{R \, T_V}$$

$$= \frac{44.27 \times (58 \times 0.9918) \times 990.5}{1000 \times 76 \times 0.0821 \times 295}$$

$= 1.371$ grams

m_I (amount of carbon dioxide condensed during first operation)

$= m + m' + m_B + m_T + m_V$

$= 0.012 + 0.040 + 0.034 + 0.129 + 1.371$

$= 1.586$ grams

m_{II}, the amount of carbon dioxide condensed during the second operation, was calculated in a similar manner except that m_B was omitted because the bulb (H) was closed from the rest of the apparatus during the re-filling with carbon dioxide.

The same remark with regard to m_B holds in the calculation of m_{III}, the amount of carbon dioxide condensed during the third operation.

It was found that, in this calculation,

$m_{II} = 1.772$ grams

and $m_{III} = 1.736$ grams

Hence the total amount of carbon dioxide condensed

$= m_I + m_{II} + m_{III}$

$= 1.586 + 1.772 + 1.736$

$= 5.094$ grams

The total heat required to warm up the bulb and carbon dioxide from -183.1°C. to +25°C. was found

= 1500.3 calories

And the total heat required to warm up the bulb alone from -183.1°C. to +25°C.

= 567.0 calories.

So that the total heat of carbon dioxide from -183.1°C. to +25°C.

= 933.3 calories

= $\frac{933.3}{5.094}$

= 183.2 calories per gram.

The mean of several determinations agreeing with one another to better than 0.5 per cent., gave the total heat from -183.1°C. to +24.6°C.

= 183.0 calories per gram.

From Table I the total heat of carbon dioxide from -183.1°C. to -78.5°C.

= 26.56 calories per gram.

Taking the mean specific heat of carbon dioxide gas from tables[4] as 0.19, then the total heat of carbon dioxide from 0°C. to 24.6°C.

= 4.67 calories per gram.

Hence the Total Heat of Carbon Dioxide from -78.5°C to 0°C.

= 183.0 - 26.56 - 4.67

= 151.8 calories per gram.

Now the heat required to warm carbon dioxide gas from -78.5°C. to 0°C.

= 78.5 × 0.19

= 14.9 calories per gram.

Hence the Latent Heat of Sublimation of Carbon Dioxide

Hence the Latent Heat of Sublimation of Carbon Dioxide

= 151.8 - 14.9

= 136.9 calories per gram (from and at -.78.5°C.)

From Table IV the average specific heat of solid carbon dioxide from -78.5°C to -56.2°C is 0.348, so that the heat required to warm solid carbon dioxide from -78.5°C. to -56.2°C.

= 0.348 × 22.3

= 7.76 calories per gram.

And the heat required to warm carbon dioxide gas from -78.5°C. to -56.2°C

= 22.3 × 0.19

= 4.24 calories per gram.

So that the Latent Heat of Evaporation of Carbon Dioxide

= (136.9 + 4.24) - (45.3 + 7.76)

= 88.1 calories per gram (from and at -56.2°C.)

Discussion:

As pointed out in the introduction to this thesis, the molecular latent heat of fusion is a physical constant about which much theorizing has been done to very little advantage. It is an unfortunate fact that this constant has been accurately measured only for a very few substances.

Crompton's Rule[5] does not hold even for monatomic molecules and therefore, as would be expected, is even less applicable to polyatomic ones. In general, however, the lower the temperature of the melting-point the lower is the molecular latent heat of fusion. From this point of view the value found for carbon dioxide falls in fairly well with the molecular latent heats of fusion at present known for substances whose molecules are not associated in the liquid state. For instance, comparing benzene[6] and carbon dioxide, the ratios of the molecular latent heats of fusion to the absolute melting points are respectively

$$\frac{78 \times 30.6}{276.5} = 8.6 \quad \text{and} \quad \frac{45.3 \times 44}{216.8} = 9.2$$

The results obtained for the molecular heats (at constant pressure) of solid carbon dioxide are of considerable interest. The average value for the molecular heat over the temperature range from the boiling-point (-78.5°C.) to the melting-point (-56.2°C.) was found to be 15.312, this value decreasing to 12.496 over the lower range of -115.0°C. to -78.5°C. The striking fact is that both these values are much larger than the molecular heat obtained for carbon dioxide in combination at much higher temperatures.

For example, the molecular heat of $MgCO_3$ is 19.1, and that of MgO is 9.8, and hence the molecular heat of carbon dioxide in combination in magnesium carbonate is 9.3. Similarly the molecular heat of $ZnCO_3$ is 21.4 and that of ZnO is 10.26, so that the molecular heat of carbon dioxide in combination in zinc carbonate is 11.14. Or, in general, the average molecular heat of compounds such as RCO_3 is 20.7 and that of the oxides RO is 11.1, so that the average molecular heat of carbon dioxide in combination is 9.6[7].

This shows that pure carbon dioxide in the solid state is held in quite a different manner from carbon dioxide in combination (say with the metal oxides). The molecules in the solid state are not held together as firmly as they are when in compounds.

In corroboration of this fact it was noticed that solid carbon dioxide has a much greater thermal expansion coefficient near its melting-point than is ordinarily attributed to a solid. Exact measurements of this expansion coefficient are at present being made but have as yet not been completed. A description of the preliminary work that has already been done in this connection will be found in the Appendix.

When this coefficient of expansion of the solid carbon dioxide has been measured it will be possible to calculate the molecular heat at constant volume. The large thermal expansion of the solid may account for the large value obtained for the molecular heat. It is expected that the molecular heat at constant volume will have the normal value.

The abnormality of the solid is also shown by its high vapour pressure. Atmospheric pressure is actually reached before melting takes place.

In the liquid state carbon dioxide is apparently unassociated, because the normal value for Trouton's Constant[8] is obtained.

Trouton's Rule states that the quotient of molecular heat of evaporation and absolute boiling-point must be approximately the same for all substances, and has a value of about 20 - 22.

Now, although atmospheric pressure is reached by carbon dioxide vapour before the solid melts, the latent heat of evaporation of the super-cooled liquid at -78.5°C. can be found by subtracting the latent heat of fusion of carbon dioxide at -78.5°C. from the latent heat of sublimation at the same temperature, as follows.

Latent Heat of Sublimation = 136.9 cal.per gm.
Latent Heat of Fusion = 45.3 " "

Latent Heat of Evaporation = 91.6 cal.per gm.

Molecular Heat of Evaporation = 91.6 × 44
= 4030.4 calories

Absolute Boiling Point = 273 - 78.5
= 194.5°.

Apply Trouton's Rule -

$$\frac{\text{Molecular Heat of Evaporation}}{\text{Absolute Boiling Point}} = \frac{4030.4}{194.5}$$

$$= 20.7$$

This value (20.7) is in agreement with that for an unassociated liquid, namely 20 - 22.

In conclusion, it is interesting to compare the value obtained for the latent heat of sublimation with that calculated from the results of the vapour density measurements of J. H. Mennie[3] and the vapour pressure data of Henning and Stock[9] using the Clausius - Clapeyron equation

$$L = T(V - v)\frac{dp}{dt}$$

where L = Latent heat of sublimation
V = Specific volume of vapour at absolute temperature T
$\frac{dp}{dt}$ = Rate of change of vapour tension with temperature T
T = Absolute temperature.

Specific gravity of solid at -78.5°C.
= 1.537 gm. per $cm.^3$

Density of vapour at -78.5°C.
= 2.840 gm. per litre (J.H.Mennie[3])

Absolute temperature
= 194.5°

$\frac{dp}{dt}$ = 0.0830 atm. per degree Centigrade (Henning & Stock[9])

Then, $V = 352.0$ c.c.

$v = .65$ c.c.

$(V - v) = 351.4$ c.c.

$$L = \frac{351.4 \times 194.5 \times 83}{1000}$$

$$= 5.670 \text{ litre-atm. per gram.}$$

$= 5.670 \times 981 \times 1033 \times 10^{-7} \times 4.187$ cals. per gm.

$= 137.7$ calories per gram (from and at -78.5°C.)

This figure (137.7) compares very favourably with the result obtained directly, namely, 136.9 calories per gram.

The work embodied in this thesis was carried out under the direction of Dr. O. Maass. It has been a privilege to have worked in daily contact with such an inspiring teacher and sympathetic director.

APPENDIX

Preliminary Work on the Determination of the Coefficient of Expansion of Solid Carbon Dioxide

Introduction:

As pointed out in the theoretical considerations resulting from the work embodied in the first two sections of this thesis, the large molecular heat of solid carbon dioxide over the temperature range between the boiling-point and the melting-point as compared with the molecular heat of combined carbon dioxide in the solid state at a much higher temperature points to the fact that free carbon dioxide in the solid state may have a large coefficient of expansion.

Experiments in this direction are at present in progress, and the prospect of an early and successful termination to the work has made it seem fit to include in this paper an account of the preliminary experiments that have been made.

Method:

The general method employed in these tests is to condense a definite weight of carbon dioxide in a small glass bulb fitted with a graduated capillary tube. A definite weight of gas is then condensed in the bulb as a liquid, completely filling the bulb and part of the capillary tube, which is then sealed off.

The position of the liquid in the capillary tube is read at different temperatures from the graduations on the glass. Then, knowing the weights of carbon dioxide and of liquid respectively, and the densities of the liquid at the various temperatures, it is possible to calculate the densities of the carbon dioxide at these temperatures. From the values so obtained the coefficient of expansion of solid carbon dioxide at various temperatures can be calculated.

Apparatus:

The apparatus for the condensation of the carbon dioxide and the liquid is the same as that used in the "Determination of the Total Heat of Carbon Dioxide from -78.5°C. to 0°C." A distilling flask (O) for the liquefied gas, together with taps (P) and (Q), was sealed to the apparatus between tap (M) and the water-trap (see Figure III).

The gas is kept liquefied by surrounding the distilling flask with solid-carbon-dioxide - ether mixture or with liquid air, depending on the gas in use.

The density bulb has a volume of about 3.5 c.c. and is glass-sealed to the apparatus in the position occupied by the bulb (H) in Figure III.

The graduated capillary tube has been carefully calibrated.

Preliminary Work:

Some tests were made on the solubility of carbon dioxide in low boiling gasoline (B.P. $<$ 35°C.). The gasoline was cooled with solid carbon dioxide and was then drawn through a filter of linen and glass wool into lime-water. There was no indication of the solubility of carbon dioxide. Gasoline was, however, abandoned as a liquid suitable for these measurements because of its variable composition.

These tests did indicate, however, that a hydrocarbon would be a suitable filling liquid for the density bulb, so that liquefied propylene was the next substance tried. It was made by removing a molecule of water from propyl alcohol by heating to 370°C. in the presence of alumina. The propylene was washed free of propyl alcohol by bubbling through water and was purified by repeated distillation. The pure propylene was then distilled into the flask (O), which was afterwards sealed off from the air.

Carbon dioxide and propylene were condensed in the density bulb, which was finally sealed off and removed from the apparatus.

It was then found that carbon dioxide was appreciably soluble in liquid propylene because on removing the bulb from a solid-carbon-dioxide - ether mixture to liquid air it was possible to watch the growth of carbon dioxide crystals from the solvent propylene at the lower temperature. These crystals disappeared again on replacing in the solid-carbon-dioxide - ether mixture.

The difficulty is now being overcome because a saturated hydrocarbon is proving very satisfactory and density determinations are at present being made with propane as the filling liquid in the density bulb.

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