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THE FREE ENERGY OF FURFURAL AND SOME OF ITS DERIVATIVES

by

PHARIS MILLER

A Thesis Submitted to the Graduate Faculty

for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

IOWA STATE COLLEGE
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ACKNOWLEDGMENT

The writer expresses his appreciation to Dr. F. E. Brown for suggesting the problem and for his encouragement during the investigation.

INTRODUCTION

The preparation and hydrogenation of furfural have been studied as a part of the program of the utilization of agricultural waste. Several investigators have published methods for the hydrogenation of furfural. Furfural was first hydrogenated by Kaufmann and Adams.(16) Among the more important later researches have been those of Adkins and Connor,(1) Adkins and Cramer,(2) Connor, Folkers, and Adkins,(6) and Komatsu and Masumoto.(20) Hydrogenated furfural products have promise of fulfilling an economic demand. It would therefore be desirable to know the optimum conditions for hydrogenating furfural.

Only part of the thermochemical data necessary to make these calculations has been obtained.(24)(31) This investigation was undertaken to determine the data needed to indicate the most favorable conditions for the hydrogenation of furfural. It was also desirable to determine the possibility of combining the production of furfural, from corn cobs or oat hulls, and the hydrogenation process in one step. Some preliminary data, obtained from chemical reactions, concerning the decomposition and stability of materials used in this combined process have already been obtained in this laboratory.(25)(14)

Some chemical reactions have a greater tendency to take place than others. The measure of this driving tendency is the free energy change of the chemical reaction.(26)(31) Knowledge of the free energy change in a proposed chemical reaction will tell the possibility of the occurrence of the reaction.

The third law of thermodynamics states that the entropy of a pure substance in its most stable form is zero at absolute zero.(19) This makes it possible to regard entropy as a definite quantity as any change in entropy would be measured from the zero value at absolute zero. The entropy of a substance at 298.16° absolute, the standard reference temperature, is given by the expression

$$\Delta S_{298.16} = S_{298.16} - S_o = \int_{o}^{298.16} \frac{CpdT}{T}$$

where Cp is the heat capacity at constant pressure, S is the entropy and the temperature is called T. The heat capacity, Cp, is zero at the absolute zero and increases with the temperature. This integral is evaluated by graphical methods, Cp being experimentally determined from as low a temperature as possible to approximately room temperature, or exactly, 298.16°K, where K stands for degrees absolute.

The utilization of this result, ΔS, in the equation

$$\Delta F = \Delta H - T\Delta S$$

makes it possible to determine ΔF, the free energy change. Here ΔF may be considered to be the negative of the maximum work available and ΔH the heat adsorbed in a reaction at constant pressure. ΔH for a compound is found by subtracting the heat of combustion of the compound from the heat of combustion of the elements in the compound. It is necessary to know the heat of combustion of a compound in order to determine the free energy change of its formation by the use of the third law of thermodynamics.

The free energy of a chemical reaction is found by the algebraic combination of the free energies of the substances taking part in the reaction.

In this paper the standard free energy at 25° is calculated for: the formation of furfural from d-xylose, the hydrogenation of furfural to form furfuryl alcohol and pentane 1, 5 diol, and the hydrogenation of furfuryl alcohol to form tetrahydrofurfuryl alcohol.

The standard free energy at 25° is the free energy of formation of one mole of substance with the products and reactants present in their respective standard states. A pure liquid or solid is in the standard state. Hydrogen gas present at a partial pressure of one atmosphere is in its standard state.

EXPERIMENTAL

Heat of Combustion

Apparatus

The heat of combustion was found by burning the compound in an Emerson fuel calorimeter. It consisted of a bomb, a calorimeter bucket and a large water jacket. The bomb had a capacity of 500 ccs. It consisted of two heavy steel hemispheres, a lead gasket and a large nut which held the hemispheres against the gasket. The hemispheres were fitted with a removable gold lining. The upper hemisphere was penetrated by a needle valve to admit oxygen into the bomb. The lower hemisphere was penetrated by an insulated wire. This wire, with the body of the bomb acting as the other terminal served to ignite the charge by melting an iron ignition wire. A deep platinum dish, suspended in the lower hemisphere, was used to hold the sample. The deep dish served to prevent loss of a liquid sample from splattering when it was ignited. The calorimeter bucket was a cylindrical thin walled metal vessel which had a capacity of 2050 ccs. of water and the bomb. It was fitted with a vertical tube containing a paddle wheel stirrer. A special stirring motor was used. When the paddle was rotating water was drawn in at the bottom and discharged at the top. The temperature of the water was determined by a Beckman thermometer on which was mounted a sliding magnifier. The calorimeter bucket sat on an insulator in the bottom of the large water jacket which surrounded it and the bomb. The jacket was filled with water to maintain a constant temperature around the calorimeter. The whole apparatus was inclosed in a large box made of insulation board and provided with a window for making the necessary observations.

Preparation of Materials

The heat of combustion of the benzoic acid used had been determined by the Bureau of Standards. Its heat of combustion at constant volume when weighed in air against brass weights was 6,329 calories per gram.

A supply of furfural was prepared by drying over anhydrous sodium sulfate for several days and then fractionally distilling at low pressure. The distillation was carried on under an atmosphere of hydrogen to prevent any oxidation of the furfural. Each sample of furfural was freshly dried and distilled just before use. The samples were water white and boiled at 60°, under 17 mm. pressure. Only the middle third of the distillation product was used in the determinations.

Furfuryl alcohol was obtained from the store room and subjected to several vacuum distillations and purified and dried in a manner similar to furfural. Its boiling point was 75° under 16 mm. pressure.

Pentane 1, 5 diol was prepared by first synthesing pentamethylene bromide.(13) Then the diactate was formed by the use of silver acetate and this was hydrolyzed by using a 2 N. solution of KOH.(10) Another sample was prepared by hydrolyzing pentamethylene diacetate with a calcium hydroxide paste.(4) Pentane 1, 5 diol, or pentamethylene glycol, boiled at 134° under 12 mm. pressure and 235°-237° at 760 mm. These values agree with the values reported in the literature.(9)(10)(16)(29) The di-p-nitrobenzoate derivative melted at 104°-105°. The value reported in the literature is 104°-105°.(9) The bis phenyl urethane derivative melted at 172°. The value reported in the literature is 174.(29)

The oxygen used in the combustions was Airco. It was over 99.5

per cent pure. The impurities consisted of nitrogen and the rare gases of the atmosphere. No combustible oils were present in the oxygen as the manufacturers use only water in lubricating the compression pumps.

Method of Procedure

The benzoic acid was made into pills weighing about 1 gram each. On burning, one of these pills caused the temperature of the calorimeter to rise approximately 2.5°. A weighed piece of pure iron ignition wire 10 cm. long was melted into a pill benzoic acid by sending a small current through it and pressing the wire into the pill. The wire and the benzoic acid were then weighed together and placed in the bomb. The ignition wire was connected to the terminals inside the bomb, making certain that no short could occur. Two ccs. of water were placed in the bottom of the bomb to saturate the bomb with water vapor. The bomb was assembled. It was then placed in a holder and connected to the oxygen tank and a gage. Oxygen was added gently at first and then as the pressure rose the valve was opened further until the pressure was 25 atmospheres. In order to flush out the atmospheric nitrogen in the bomb the oxygen was allowed to escape until the pressure in the bomb was equal to the atmospheric pressure. The bomb was filled a second time to 25 atmospheres.

The bomb was then lowered into a transparent container of water and watched to observe the formation of bubbles indicating leaks. If there were no leaks the bomb was wiped dry and placed in the calorimeter bucket. Then, 1950 grams of water at 23° to 24° was added and the bucket was placed in position. The temperature of the water in the bucket was one or two degrees below the temperature of the water in the surrounding outer jacket. The stirrer was then lowered into the water. The thermometer was placed in position. Neither the stirrer nor the thermometer touched the bomb.

The stirring motor was started. Rapid heat transfer is most desirable in combustion calorimetry and the stirrer was run as rapidly as was possible without splashing water. The stirrer was allowed to run for a few minutes to insure thermal equilibrium between different parts.

The temperature was observed until the rise per minute had reached a uniform rate. Then the reading of the thermometer for the preliminary warming up period was taken at one minute intervals for five minutes and on the fifth reading the firing switch was closed for three seconds. A potential difference of 12 volts was secured by introducing suitable resistance in the 110 volt circuit.

The thermometer was read each minute while the temperature of the calorimeter was rising. If data in calorimetry are to be comparable the periods of rise must be the same. In this work an effort was made to adjust the weight of charge so that the maximum temperature was reached in five or six minutes. The results of any other temperature rise were rejected. To find the rate of cooling after the maximum temperature was reached the temperatures were recorded for five minutes.

The transfer of heat due to radiation must be determined by calculation. Radiation was corrected for in this investigation by using Dickinson's method.(8) This method separates the heating period into two parts, the first 0.6 and the last 0.4. The 0.6 point is reached from one to one and one-half minutes after the firing. To determine the exact point the temperatures were taken at five second intervals during this half minute.

The temperature rise was from two to three degrees so that the final temperature was within one degree of the water jacket temperature. Under these conditions the corrections for the heat gained or lost to the surroundings is at a minimum.(8)

The bomb was taken out of the water. The oxygen pressure released and the inside of the bomb inspected for unburned residue. If a liquid was to be burned in the bomb it was placed in a small Erlenmyer flask, fitted with a rubber stopper having a medicine dropper passing through the center. The dropper was used to transfer the liquid to the combustion pan, and the weight of the liquid used was obtained by difference.

Calculations

The standard sample of benzoic acid was used to find the heat capacity of the bomb and the calorimeter bucket. The apparent water equivalent of the bomb was obtained by subtracting the heat in calories needed to produce the rise in temperature of the weight of water used from the heat produced by burning the benzoic acid. The difference was the heat absorbed by the metal bomb and bucket.

The manner of finding the correct temperature rise is given below:

The heat produced by combustion caused the temperature of the bomb and the water in the calorimeter bucket to rise above its surroundings. The rise caused a loss by radiation. Consequently, the temperature increase was not quite as much as it should have been. This effect was minimized by having the temperature of the bomb and the water in the calorimeter bucket lower than its surroundings before the combustion. There were, therefore, two corrections to apply: the warming effect at the start and the cooling effect at the end. The method used by Dickenson assumes that under the conditions used in this investigation the absorption of heat is continued during six-tenths of the total rise and that heat is lost during the remainder of the rise in temperature.

In one determination the reading at firing was 1.191°; in one minute 2.77°; in one minute and five seconds, 2.80°; in one minute and ten seconds 3.00°; in five minutes a maximum was reached at 3.868°. The total rise was 2.677. Six-tenths of 2.677° is 1.606°. When a rise of 1.606° had occurred the reading was 2.797°. The time required for this rise was nearly one minute and five seconds or 1.083 minutes. For 1.083 minutes the warming correction was added and for the remainder of 3.917 minutes the cooling correction was applied.

In this determination the average warming rate per minute is 0.0046. This is multiplied by 1.083 and added to the initial, or firing temperature, to give the corrected initial temperature. The average cooling rate was 0.0014, and this, times 3.917 added to the maximum temperature, gives the corrected final temperature. These data and the calculation of the heat of combustion for pentane 1, 5 diol based on these data are used in the following sample calculation:

Weight of iron ignition wire burned = 0.0121 gm.

Weight of pentane 1, 5 diol used = 0.8637 gm.

Time	Thermometer reading	
0	1.168	$\frac{1.191 - 1.168}{5} = \frac{0.023}{5} = 0.0046$
1	1.173	
2	1.178	average change per minute is 0.0046
3	1.182	
4	1.187	
5	1.191	firing temperature
1	2.77	
1.083	2.80	time at 0.6 of the total rise
2	3.61	
3	3.81	
4	3.86	
5	3.868	maximum temperature
1	3.868	$\frac{3.868 - 3.856}{5} = \frac{0.012}{5} = 0.0024$
2	3.864	
3	3.862	average change per minute is 0.0024
4	3.860	
5	3.856	

Radiation correction:

Corrected Final Temperature = 3.868 + (0.0024)(3.917) = 3.877

Corrected Initial Temperature = 1.191 + (0.0046)(1.083) = $\underline{1.196}$

2.681

Corrected Temperature Change

(temperature rise)(weight of water + water equivalent of calorimeter) = (total heat obtained)

$$(2.681)(2401) = 6446.7 \text{ cals.}$$

Heat of combustion of iron wire = 19 cals.

6446.7-(heat of combustion of iron wire) = 6430.0 cals.

$$\Delta H = (6430.0)\,\frac{\text{mole weight}}{\text{weight sample}} = (6430.0)\frac{(104.1)}{(0.8837)}$$

$$= 756.7 \text{ Kg cals. per mole } C_5 \text{ pentane 1, 5 diol}$$

Results

Table I gives the results of the standardizations. The water equivalent of the calorimeter was found to be 450 calories.

Table II shows the results obtained from burning furfural. The heat of combustion at constant volume was 558.3 kilogram calories per mole.

Table III contains the results obtained for the heat of combustion of pentane 1, 5 diol at constant volume. The value was 752.3 kilogram calories per mole.

TABLE I

Heat of Combustion Data.
Results of Standardization of the Oxygen Bomb Calorimeter.

Water Equivalent of the Bomb			
Run Number	Equivalent in calories	Run Number	Equivalent in calories
1	488	13	431
2	465	14	432
3	440	15	447
4	435	16	466
5	507	17	432
6	462	18	415
7	461	19	446
8	492	20	459
9	436	21	448
10	500	22	432
11	430	23	428
12	456	Av. value =	450.0

TABLE II

Heat of Combustion of Furfural

Run Number	ΔHC_v	Run Number	ΔHC_v
1	550.0	5	562.0
2	563.3	6	557.0
3	549.8	7	562.0
4	554.2	Av. value =	558.3

TABLE III

Heat of Combustion of Pentane 1, 5 diol

Run Number	ΔHC_v	Run Number	ΔHC_v
1	752.0	4	748.0
2	753.8	5	756.6
3	752.0	Av. value =	752.3

Heat Capacity

Apparatus

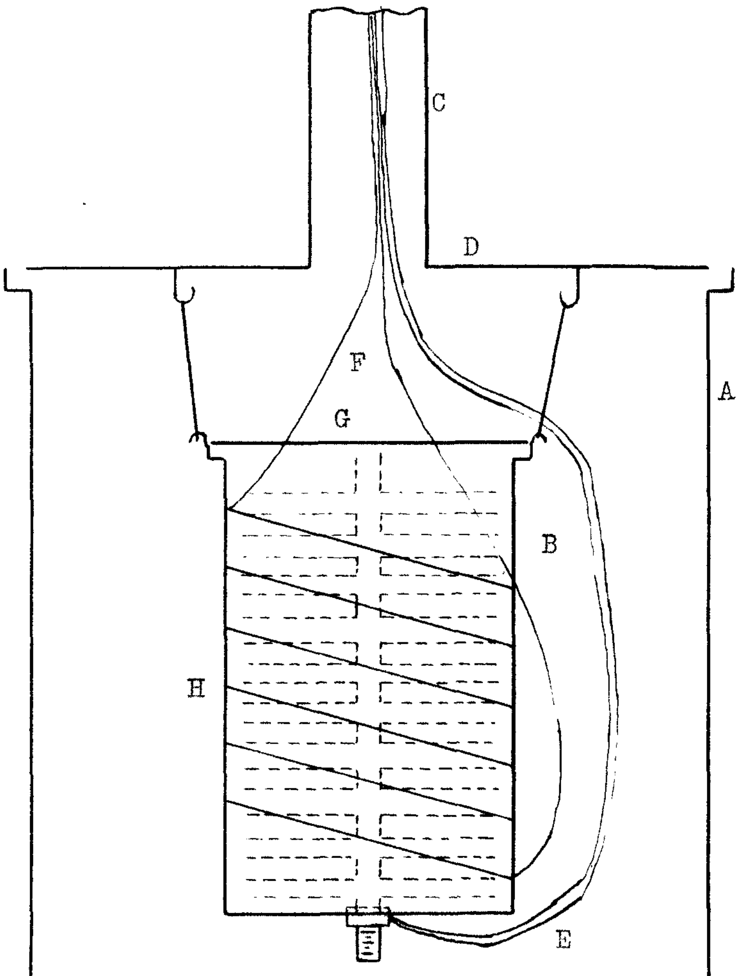
The heat capacities were determined by placing samples in a brass cylinder and measuring the electrical energy required to raise the temperatures while the cylinder was protected from radiations of heat by being surrounded by an area of very low pressure. The apparatus was essentially the same as that used by other investigators(11)(12)(22)(28)(30). Diagram I is a representation of the calorimeter. It consists of two principal parts - an outer and an inner cylinder, A and B, respectively.

The outer cylinder was 15 cm. long and 8 cm. in diameter. It was made of brass coated on both sides with solder to decrease its permeability. The lid of the outer cylinder, D, was removable. It was perforated at its center, and a monel metal tube, C, 30 cm. long and 1 cm. in diameter was soldered around the hole. This tube served as a connection to the vacuum train and through it passed the wires E and F. The cover also bore three hooks from which the inner cylinder was suspended by silk threads. The inner container was 7.5 cm. long and 3.7 cm. in diameter, was made of brass and weighed 50 grams. It had a capacity of 60 cubic centimeters. Its removable lid, G, was soldered on by means of Wood's metal.

Inside the container was a removable center piece, I, fitted with 20 thin copper vanes. These vanes were soldered to the center piece. The vanes were to insure as even, complete and rapid distribution of heat throughout the container as possible.

Wrapped around the calorimeter can, B, was a heating coil, H, composed of 125 cms. of No. 31 constantan wire. Constantan wire was chosen

Diagram I



The calorimeter used for the determination
of heat capacities.

in order to keep the resistance of the wire as constant as possible through the temperature range. The coil was wound on the cylinder, coated with Bakelite varnish and baked on. Its resistance, measured by a wheatstone bridge was 16 ohms at 25°. The wires, F, were led into the container through de Khotinsky cement and were soldered to the heating coil. The wires of the thermoelement, E, were brought into the system in the same manner and the element was soldered to a small flat piece of copper which was fastened to the calorimeter by screwing a nut onto a bolt soldered to the bottom of the container. The thermoelement was made of No. 31 constantan and No. 28 copper wires. The junctions were made by fusing the wires together. The wires selected were tested for homogeneity by passing them through a U-tube kept in liquid air. No electromotive force was produced between different parts of the wire. The thermoelement was protected from atmospheric corrosion by coating the entire length of the wire with Bakelite varnish.

The thermoelement was aged by alternately cooling in liquid air and warming to room temperature. It was calibrated at the boiling point of water,(21) the transition point of sodium sulfate, 32.38°C(21) the ice point, the freezing point of mercury, -38.87°C(21) the sublimation point of carbon dioxide, -78.47°C(15) and the boiling point of liquid oxygen, -182.96°C(15). These points gave a straight line deviation from the International Critical Table values.(21)

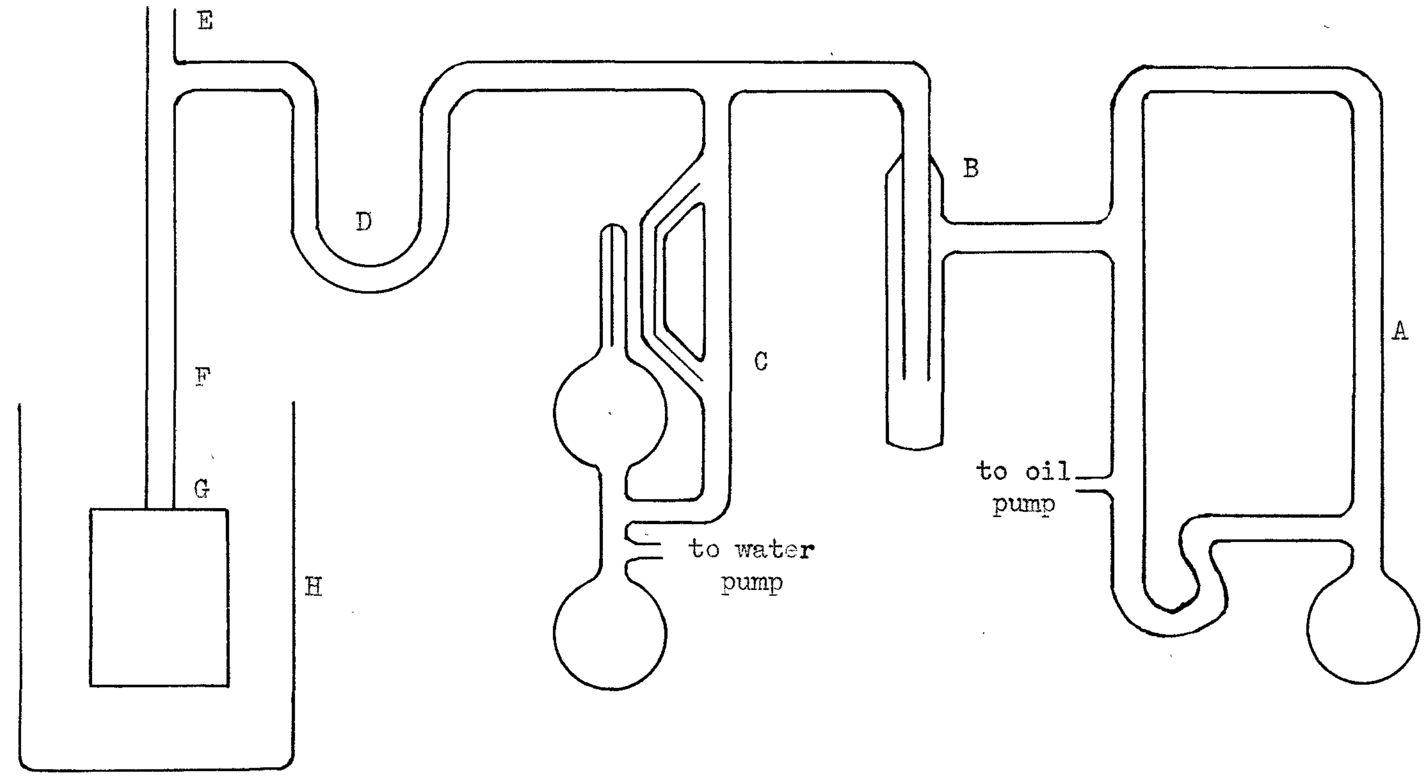
The potential created by the thermoelement was measured by means of a Leeds and Northrup student potentiometer and a type P galvanometer, which had a specially wound movable coil designed for use with a thermoelement. The coil had a resistance of 35 ohms, and a sensitivity of 1.5 microvolts.

The voltage drop across the heating coil was measured by means of a student potentiometer, in conjunction with a specially wound tapped resistance coil, or volt box.

The electrical current supplied to the heating coil was furnished by two storage batteries kept fully charged by a trickle charger. The voltage drop across the heating coil was regulated by a 100 ohm sliding rheostat of the conventional type and a special rheostat of low resistance. This rheostat was made according to the directions given by Daniels, Matthews and Williams, and consisted of a constantan wire dipping into a test tube of mercury.(7) The length of the wire above the surface of the mercury could be accurately adjusted and the voltage drop across the heating coil kept constant.

Diagram II represents the vacuum train connected to the calorimeter. The vacuum train consisted of two principle parts, a mercury diffusion pump, A, and a McLeod gage, C. The mercury diffusion pump, A, was backed by an oil pump. It was capable of maintaining a pressure of 0.1 micron in the system. The mercury diffusion pump, A, was connected through a trap, B, to the McLeod gage, C. The gage was connected through a trap, D, to the monel metal tube, F. The monel metal tube, F, lead to the outer container, G; the container, G, is surrounded by a large Thermos flask, H, and the Thermos flask, H, held the material used to cool the calorimeter, either solid carbon dioxide or liquid air. The traps B and D were surrounded with either solid carbon dioxide or liquid air. Their purpose was to freeze out the mercury vapor, preventing mercury

Diagram II



The High Vacuum System Connected to the Calorimeter and the Vacuum Flask Surrounding the Calorimeter.

molecules from reaching the calorimeter where they might cause increased heat conductivity.

Preparation of Materials

The apparatus for determining specific heats was standardized by the use of J. T. Baker's analyzed naphthalene.

Furfural, furfuryl alcohol and pentane 1, 5 diol were prepared in the same manner as described under preparation of materials for heats of combustion.

The sample of tetrahydrofurfuryl alcohol was generously supplied by Dr. Henry Gilman, of Iowa State College. The boiling point of 83°C under 24 mm pressure remained unchanged on drying over anhydrous sodium sulfate and vacuum distilling. Tetrahydrofurfuryl alcohol is quite stable and it is not necessary to freshly distill it each time before use.

The dextro-xylose was from the Pfanstiehl Chemical Company, Waukegan, Illinois.

Method of Procedure

The apparatus was calibrated by using the data of Southard and Brickwedde.(34) The apparatus was filled with naphthalene and heated over two temperature ranges. In the first range the outer container was surrounded with solid carbon dioxide and in the second with liquid air. The temperature range covered in the first instance was from -78.5° C to 0°C, or to 25° if the specific heats of the compounds at this temperature were not already known. In the second instance the temperature range was from -180° to approximately -60°C so that an overlapping of the two determinations would serve as a check on each other. Diagram III shows the standardization over the two ranges. The standardizations were made in the manner described below.

In making a determination the inner container or calorimeter can was first filled with the compound and surrounded with a crushed ice mixture. The top was then fitted on and soldered into place using Wood's metal alloy as a solder and a solution of three parts zinc chloride and one part ammonium chloride as a flux. The parts to be soldered were kept well tinned with ordinary solder. The temperature was kept low to prevent the decomposition of the compound.

A small vent hole in the top was soldered last so that no air pressure could be built up in the container. Records were kept of the weight of material used and of the weight of the container and solder so that if the weight of solder and calorimeter were not the same as in the calibration a correction could be applied in calculating the results.

The heating wires were then soldered on and the thermoelement attached. The calorimeter was then suspended from the outer container and placed in the outer jacket. The cover of the outer jacket was soldered while the body of the container was held in water so that the temperature of the inner container would not be raised excessively. A piece of glass tubing was cemented into the monel metal tube by means of de Khotinsky cement. This glass tube was then sealed to the low pressure system. The apparatus was then tested for leaks. When a pressure of 0.1 micron was maintained, the cooling mixture was placed around the outer container. Hydrogen was slowly admitted to the apparatus and the calorimeter allowed to cool. Hydrogen was used because it is a good conductor of heat and establishes temperature equilibrium rapidly. It will not condense at the standardization over the two ranges. The standardizations were made in the manner described below.

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After the system had reached equilibrium with the liquid air or solid carbon dioxide it was again evacuated. When the pressure had fallen to 0.1 micron the calorimeter was ready for the determination.

The heating rate was adjusted by a preliminary run so that in each determination the temperature range was covered in about 60 minutes. Some compounds had a transition point and as the transition temperature was approached the heat input was increased so that the time spent at the transition point did not increase the total heating time. To insure a steady current from the batteries a preliminary resistance of the same size was connected to them for a time before they were switched to the heating coil.

The time was measured by a Hammond electric clock, which permitted considerable attention to be given to keeping the voltage drop across the coil constant and to following the temperature change with the thermoelement.

Thermoelement readings were taken every minute. Pressure readings were taken every three to five minutes. The voltage drop was constantly adjusted except when these readings were being taken. Readings were continued after the current was turned off to observe any heat lag and the rate of cooling. The conversion of the thermoelement reading in microvolts to absolute temperature was made by means of a large graph which could be read to 0.1 degree. Diagram IV shows the thermoelement curve obtained by plotting microvolts against absolute temperature (thermodynamic scale). The heat capacity of each substance was determined by at least two experiments and usually by three or four experiments over each temperature range.

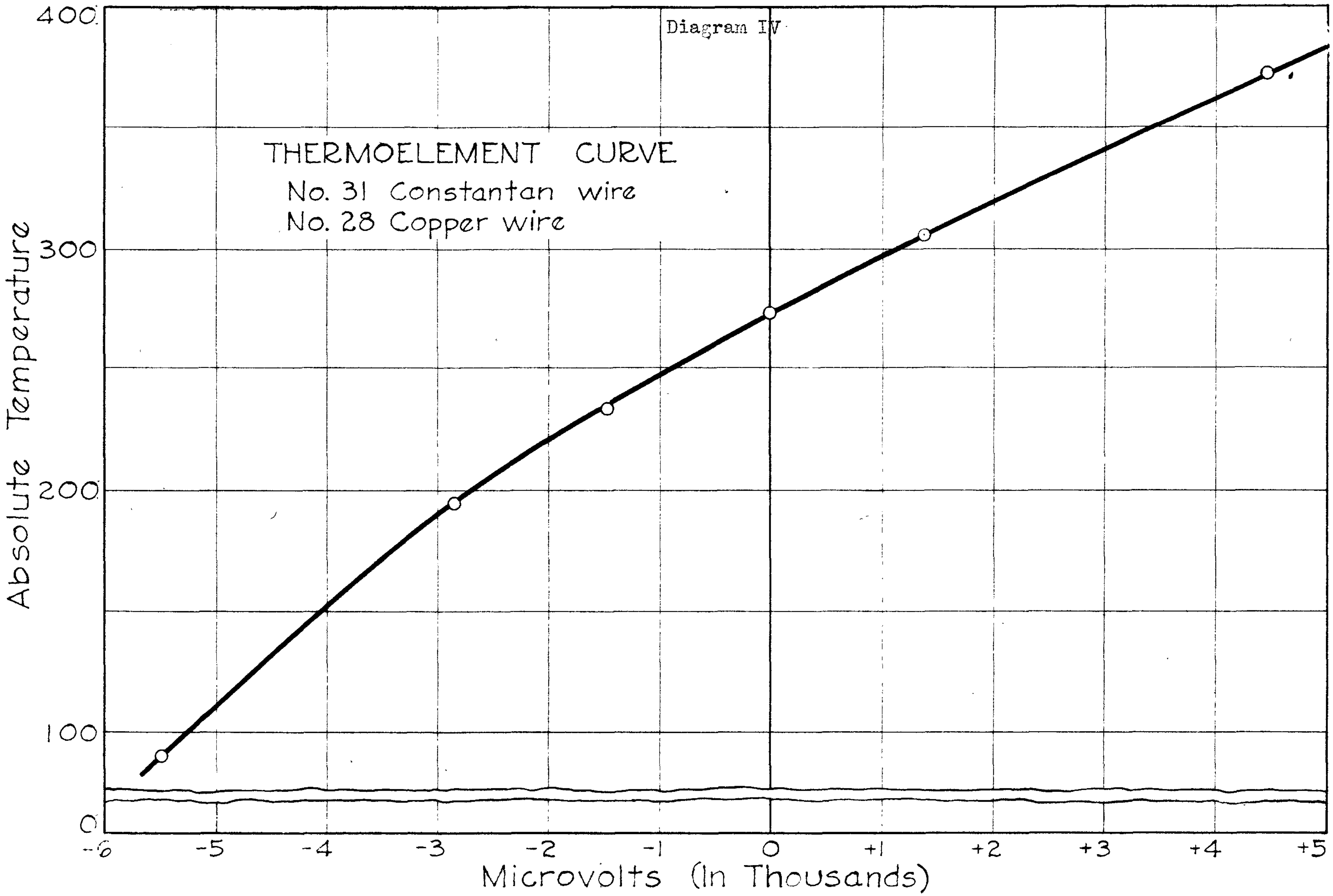


Diagram IV
THERMOELEMENT CURVE
No. 31 Constantan wire
No. 28 Copper wire
Absolute Temperature
400
300
200
100
0
Microvolts (In Thousands)
-6
-5
-4
-3
-2
-1
0
+1
+2
+3
+4
+5

Calculation of Heat Capacity

In the determination of heat capacity for use in the calculation of the entropy it is necessary to know the actual heat capacity for each temperature increment of about 10 or 15 degrees, beacuse the slope of the heat capacity plotted against temperature is different for each compound and varies at different temperatures and for compounds such as these cannot be calculated by any equation.

The potentiometer readings were in microvolts. They were changed to absolute temperatures by means of a large chart on which one division corresponded to 0.1 degree.

The formula used for finding the heat input in calories is:

(heat in calories) = (watts)(seconds)(conversion factor electrical energy to calories)

$$\text{Heat in calories} = \frac{E^2}{R}(t)(0.2388)$$

Where R is the resistance of the heating coil
t is the time in seconds
0.2388 is the conversion factor from electrical energy to heat in calories

The conversion factor was calculated from the data of Southard and Brickwede(34); one gram calorie at 15° equals 4.1833 international joules. In the calculations the time interval was usually 300 seconds or a little longer. A calculation will illustrate the method. The data are for furfuryl alcohol. From 7:23 to 7:29, a six minute time interval, the temperature changed from 161.0°K to 176.0°K, a difference of 15°, the voltage drop was constant at 7.500 volts, substituting in the equation

$$\text{Heat input in calories} = \frac{(7.5)^2}{15.94}(6)(60)(0.2388) = 303.3$$

The average temperature was 168.5°K. The container and solder weighed

1.02 times as much as when calibrated and the calibration curve at 168.5 degrees gives the value of five calories per degree for the container. Then the heat capacity of the container is (1.02)(5)=5.1 calories. The heat required to raise the container and contents one degree is $\frac{303.3}{15} = 20.22$ calories. Subtract from this the heat required to raise the container one degree, 5.1 calories. Then 15.12 calories is required to raise the furfuryl alcohol one degree. There was 0.7143 mole of furfuryl alcohol present in the container. The molal heat capacity at 168.5°K is $\frac{15.12}{0.7143} = 21.2$ calories.

Results

Tables IV to XIII give condensed data for the heat capacity of furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, pentane 1, 5 diol and d-xylose.

The significance of the numbers in the respective columns is:

1. Absolute temperature of the calorimeter at the start of a heating period.
2. Absolute temperature of the calorimeter at the end of the same heating period.
3. The time interval in minutes.
4. The temperature increment.
5. The voltage drop across the heating coil.
6. The calories required to raise the container and compound one degree.
7. Calories required to raise the container one degree.
8. Heat capacity of the compound in calories per mole per degree.

TABLE IV

Condensed Table of Heat Capacity Data for Furfural

Outer container surrounded with liquid air
Pressure = 0.1 micron
Mole fraction = 0.7689

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
106.8	125.6	6	18.8	7.500	16.12	3.68	16.2
125.6	140.6	5	15.0	7.500	16.85	4.20	16.5
140.6	154.4	5	13.8	7.500	18.32	4.63	18.0
154.4	167.4	5	13.0	7.500	19.47	5.04	18.8
167.4	181.5	6	14.1	7.500	21.50	5.57	20.7
183.7	194.1	6	10.4	7.500	24.30	6.72	22.9
181.5	219.7	20	38.2	7.500	26.45	7.77	24.3

TABLE V

Condensed Table of Heat Capacity Data for Furfural

Solid carbon surrounding the container
Pressure = 0.01 micron
Mole fraction = 0.735

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
Δ H fusion$_{235.1}$ = 3434							
240.2	271.8	10	31.6	10.000	34.34	10.02	29.15
261.6	274.2	5	12.6	10.000	35.60	12.00	32.15

TABLE VI

Condensed Table of Heat Capacity Data for Furfuryl Alcohol

Outer container surrounded with liquid air
Pressure = 0.1 micron
Mole fraction = 0.7143

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
111.0	132.0	6	21.0	7.500	14.44	3.67	15.1
132.0	147.0	5	15.0	7.500	16.86	4.18	17.3
147.0	161.0	5	14.0	7.500	18.07	4.69	18.8
161.0	176.0	6	15.0	7.500	20.22	5.10	21.2
176.0	190.0	6	14.0	7.500	21.65	6.02	21.9
205.4	214.5	8	14.9	7.500	27.15	8.16	26.6
214.5	217.9	2	3.4	7.500	28.36	8.46	27.9

TABLE V II

Condensed Table of Heat Capacity Data for Furfuryl Alcohol

Outer container surrounded with solid carbon dioxide
Pressure = 0.1 micron
Mole fraction = 0.709

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
210.7	222.0	6	11.3	7.750	28.57	7.04	27.5
195.1	241.2	15	46.1	10.000	29.15	7.34	30.8
ΔH fusion$_{253.5}$ = 3540 calories / mole							
258.3	267.2	4	8.9	10.000	40.03	12.08	39.9

TABLE VIII

Condensed Table of Heat Capacity Data for Tetrahydrofurfuryl Alcohol

Outer container surrounded with liquid air

Pressure = 0.1 micron

Mole fraction = 0.6310

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
98.2	124.6	8	26.2	7.700	16.27	3.4	20.4
124.6	139.3	5	18.12	7.700	18.12	3.7	22.9
139.3	148.0	4	8.7	7.700	24.52	4.3	32.13
148.0	178.2	14	28.2	7.700 8.500 9.000	31.2	4.9	41.7
178.2	197.7	10	19.5	9.000	33.28	6.3	42.7
197.7	217.8	11	20.1	9.000	35.53	8.0	43.6

TABLE IX

Condensed Table of Heat Capacity Data for Tetrahydrofurfuryl Alcohol

Outer container surrounded with solid carbon dioxide
Pressure = 0.1 micron
Mole fraction = 0.6418

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
210.9	226.0	10	15.1	7.750	35.65	7.17	44.4
226.0	247.0	14	21.1	7.750	35.75	8.49	42.5
247.1	271.2	17	24.1	7.750	37.93	11.59	41.1

TABLE X

Condensed Table of Heat Capacity Data for Pentane 1, 5 diol

Outer container surrounded with liquid air
Pressure = 10.0 microns
Mole fraction = 0.1264

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Cals. det.	Cals. per mole
92.6	109.1	5	15.3	5.000	7.34	3.4	26.8	26.8
176.6	221.5	10	44.9	7.000	12.31	7.3	39.6	39.6

TABLE XI

Condensed Table of Heat Capacity Data for Pentane 1, 5 diol

Outer container surrounded with solid carbon dioxide

Pressure = 0.1 micron

Mole fraction = 0.1452

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
199.3	219.8	11	10.5	4.800 4.200 4.300	12.68	6.86	40.1
Δ H fusion$_{248}$ = 3759							
286.5	253.0	11	33.5	8.000 7.000	19.95	13.12	47.04
271.0	303.1	16	32.1	7.000	21.9	15.85	50.0

TABLE XII

Condensed Table of Heat Capacity Data for d-Xylose

Outer container surrounded with liquid air
Pressure = 3.0 microns
Mole fraction = 0.1627

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Cals. det.	Cals. per mole
95.8	125.2	6	29.4	5.500	5.55	3.4	13.2	13.2

TABLE XIII

Condensed Table of Heat Capacity Data for d-Xylose

Outer container surrounded with solid carbon dioxide

Pressure = 0.1627

Mole fraction = 0.01 micron

Temp. start	Temp. time	Time interval	Temp. increase	Volts drop	Calories per degree	Calories for container	Calories per mole
197.4	210.9	7	13.5	4.800	10.75	6.7	24.6
210.9	222.0	6	11.1	4.800	11.19	7.0	25.8
222.0	229.0	4	7.0	4.800	11.84	7.5	26.7
229.0	243.3	9	14.3	4.800	13.02	8.3	28.6
243.3	250.5	5	17.2	4.800	14.39	9.6	29.5
253.0	259.7	6	6.7	4.500	16.33	11.0	32.8
258.1	269.2	11	11.1	4.500	18.08	12.1	36.84

The complete data are shown in Graphs 1 to 5. In Graphs 1 and 2 the slope of the line at 300° was found by extrapolating the data of Andre not shown on the graphs.(3)

In calculating the heats of transition the assumption was made that increase in heat capacity just before the melting point was caused by premelting of the compound and a decrease just after the transition temperature was caused by a heat lag. The temperatures of the transition points were checked by freezing the compounds in a glass test tube and following the change with the thermoelement.

Calculating of Entropy

Graph 6 shows the values obtained by plotting Cp/T against T. The entropy was determined by graphically integrating the area under each curve. The graph shows only the area above the value 0.110; the area beneath this must be included in the calculations. The area not shown in the chart has a value of 23.96 entropy units.

Furfuryl alcohol and pentane 1, 5 diol had a transition temperature in this temperature range and the entropy change is determined by dividing the heat of fusion by the transition temperature.

The heat capacity below 100° was found by the extrapolation method of Kelly, Parks and Huffman.(17) The entropy below 90° was found by the same equation multiplied by $\frac{dt}{T}$.

The equation for extrapolating the heat capacity is

$$Cp \text{ (per mole)} = (A + BT)\, Cp^{o}$$

where Cp is the heat capacity at the temperature T and Cp^{o} is the value of the reference data given by Kelly, Parks and Huffman at the temperatures T.

One set of reference data is used for aliphatic compounds such as d-xylose and pentane 1, 5 diol and another set is used for cyclic compounds. In this calculation furfural, furfuryl alcohol and tetrahydrofurfuryl alcohol were classed as cyclic compounds. A and B are constants, the constants are found for each substance by taking the experimentally determined Cp values for each substance at two temperatures as 110°K and 120°K. These values, with the values for Cp^o and the temperatures, are substituted in two equations.

In one equation the Cp value at 110°, Cp^o for the class of substance at 110°, and the temperature (110°) are substituted. In the second equation the Cp value at 120° is substituted with corresponding values for Cp^o and T. The two equations are solved simultaneously to secure the values of A and B.

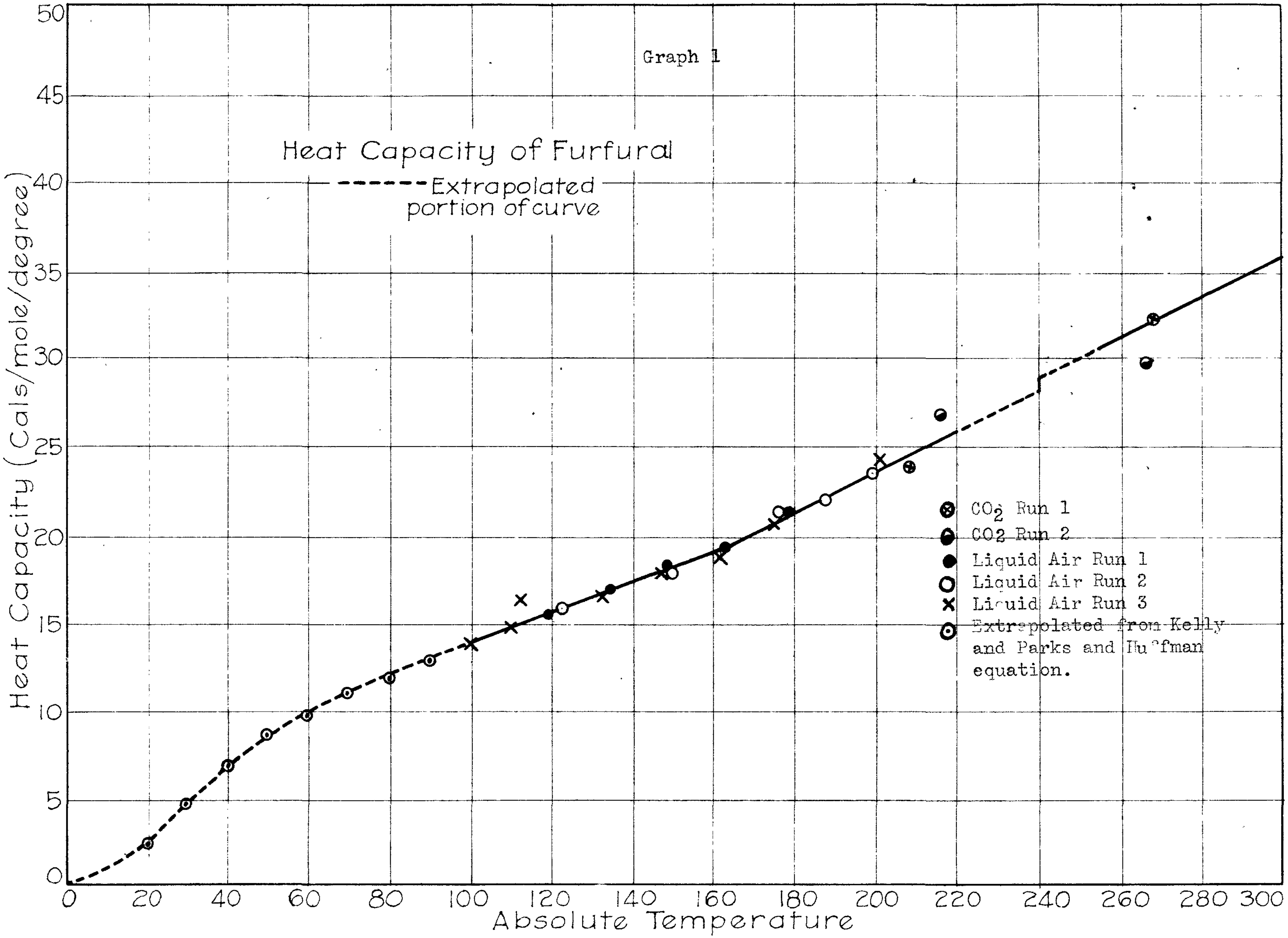
$$Cp = (A + BT)Cp^o \text{ by } \frac{dt}{T} \text{ gives}$$

$$\frac{Cpdt}{T} = ACp^o\frac{dt}{T} + BCp^o\,dt$$

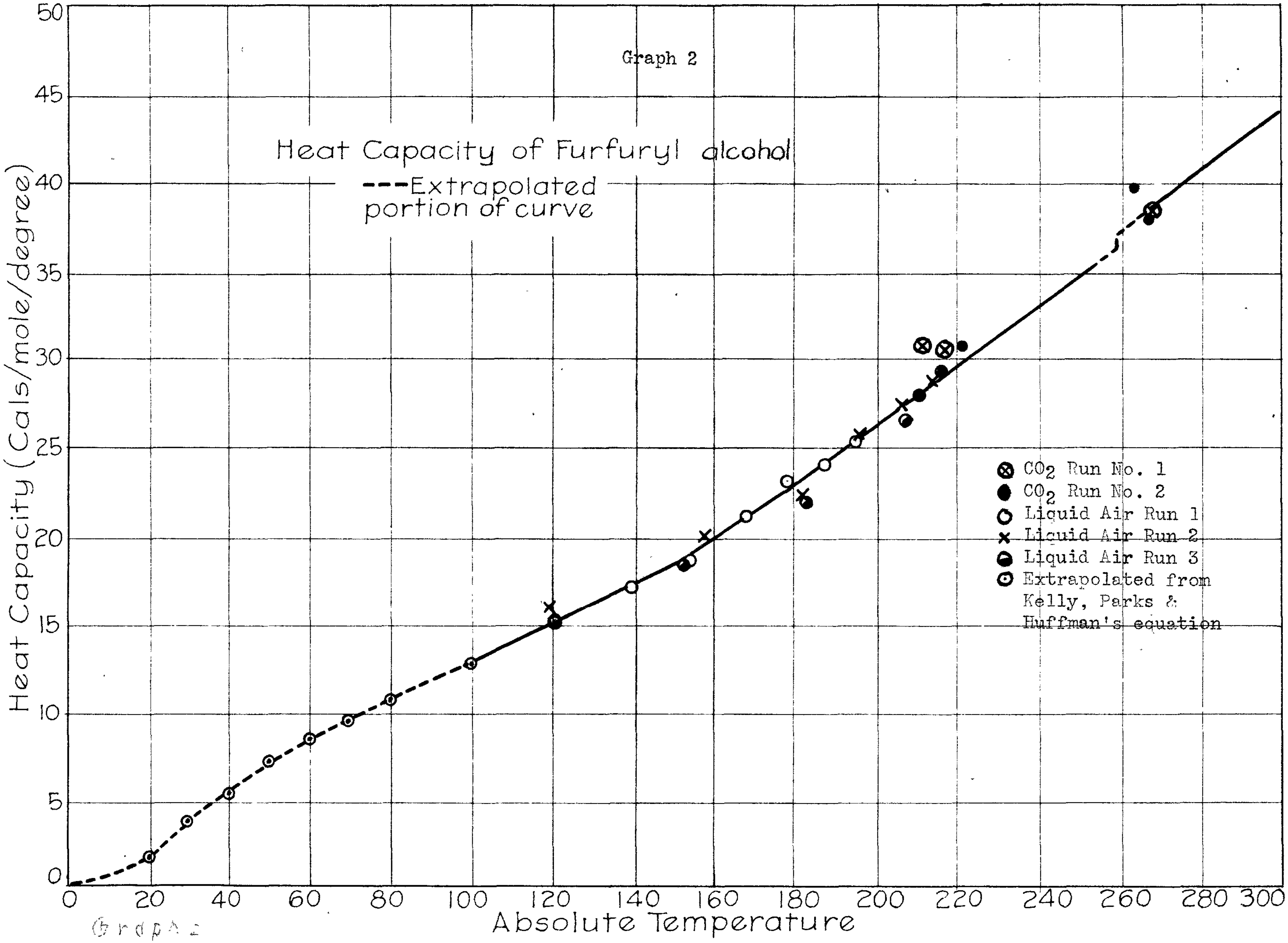
integrating and considering A and B as constants

$$\int_0^{90} \frac{Cpdt}{T} = A\int_0^{90} Cp^o\frac{dt}{T} + B\int_0^{90} Cp^o dt$$

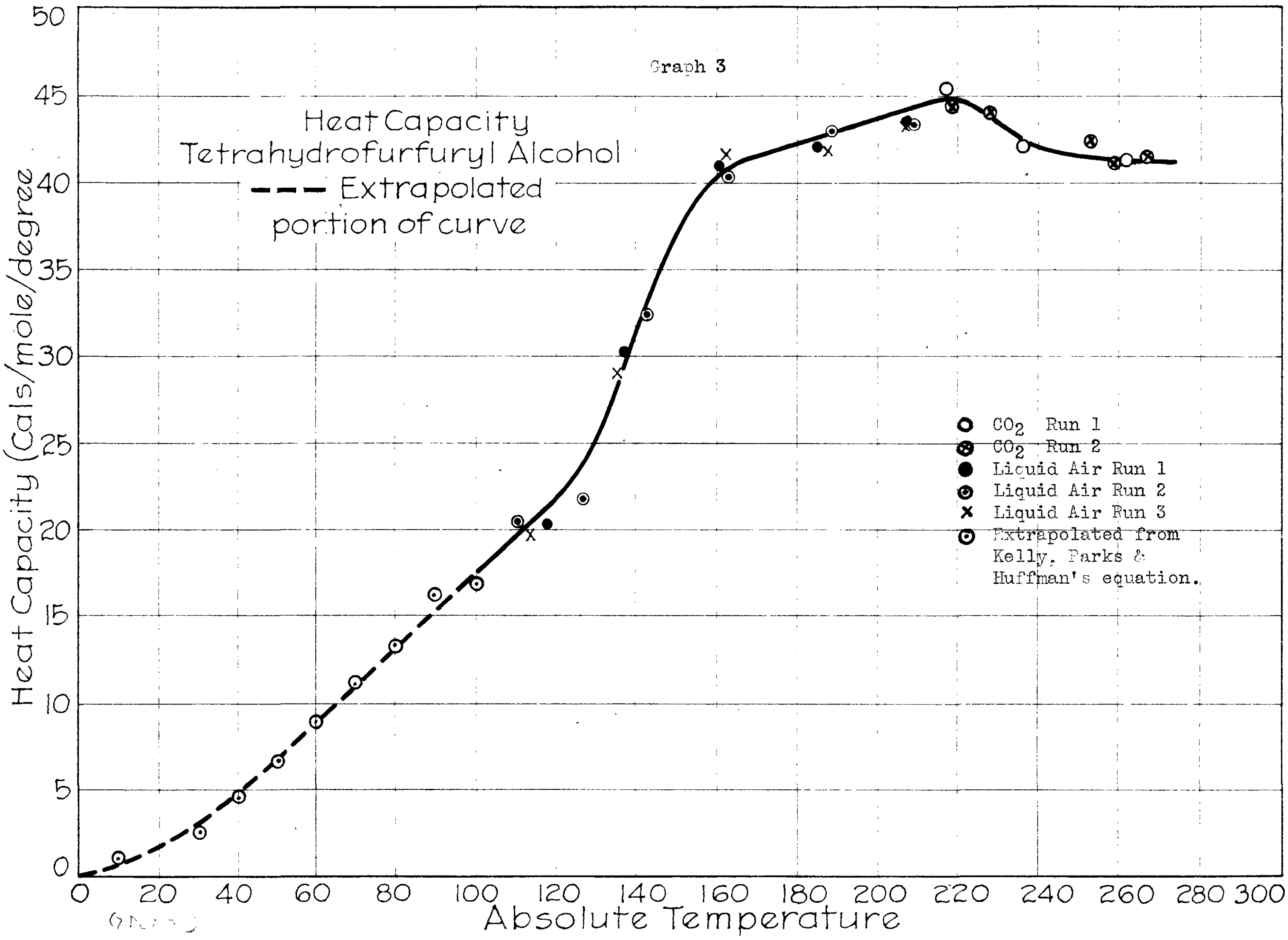
since $\Delta S = \int_0^T Cp\frac{dt}{T}$, then substituting ΔS for $\int_0^T \frac{Cpdt^o}{T}$ gives


Graph 1
Heat Capacity of Furfural
Extrapolated portion of curve
Heat Capacity (Cals/mole/degree)
0
5
10
15
20
25
30
35
40
45
50
Absolute Temperature
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
CO$_2$ Run 1
CO$_2$ Run 2
Liquid Air Run 1
Liquid Air Run 2
Liquid Air Run 3
Extrapolated from Kelly and Parks and Huffman equation.

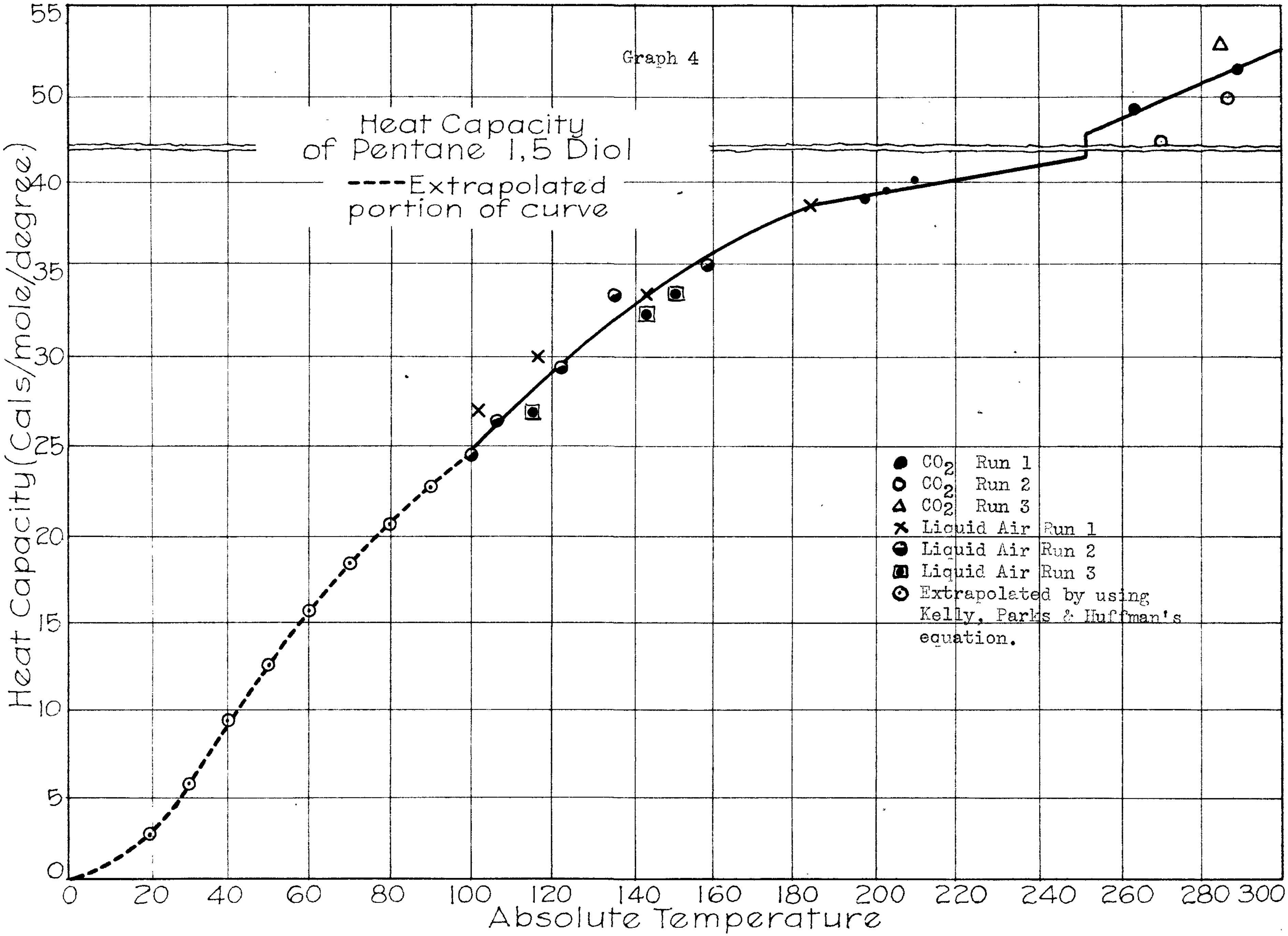
Graph 2


Heat Capacity of Furfuryl alcohol

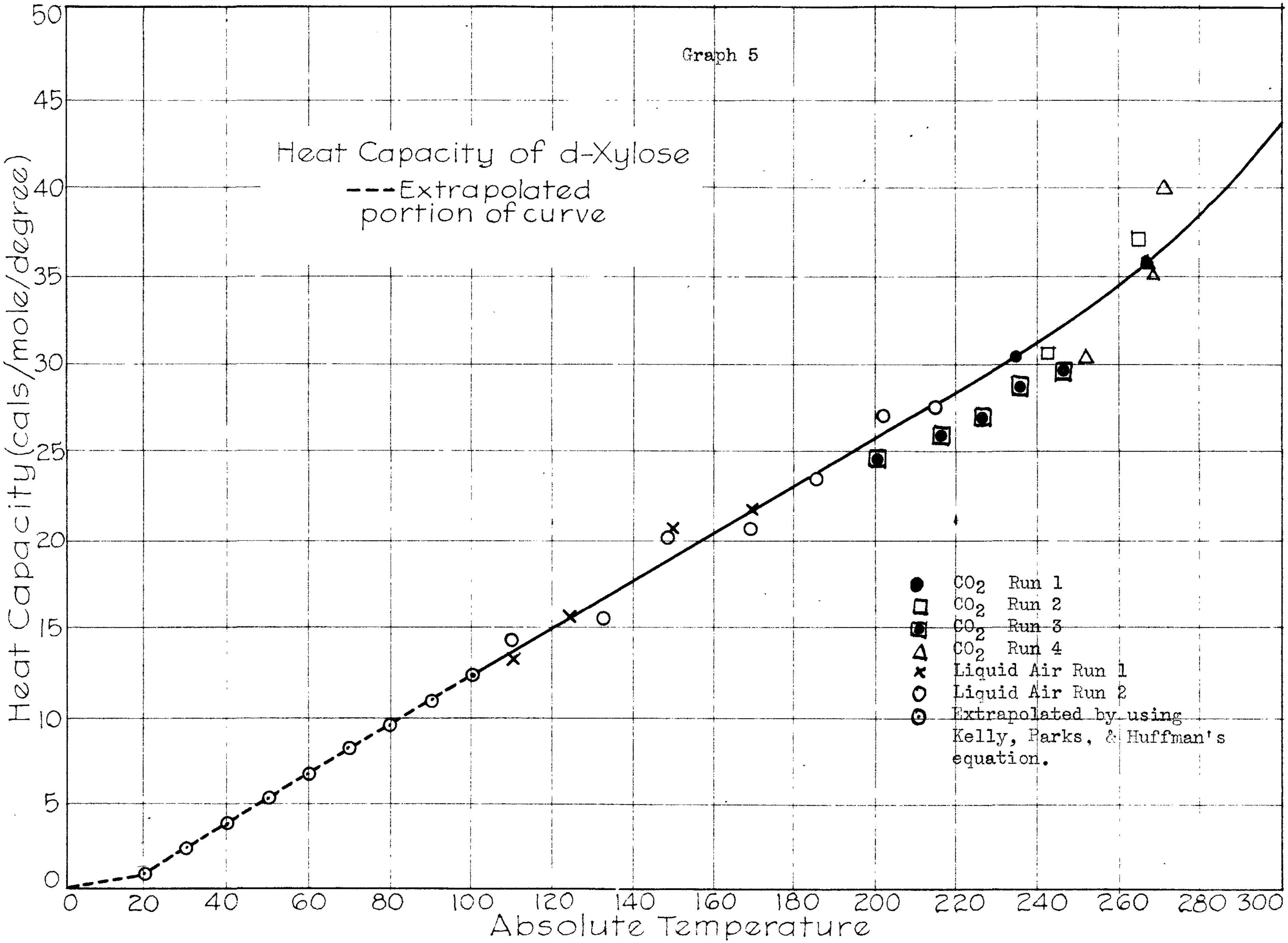
Graph 2

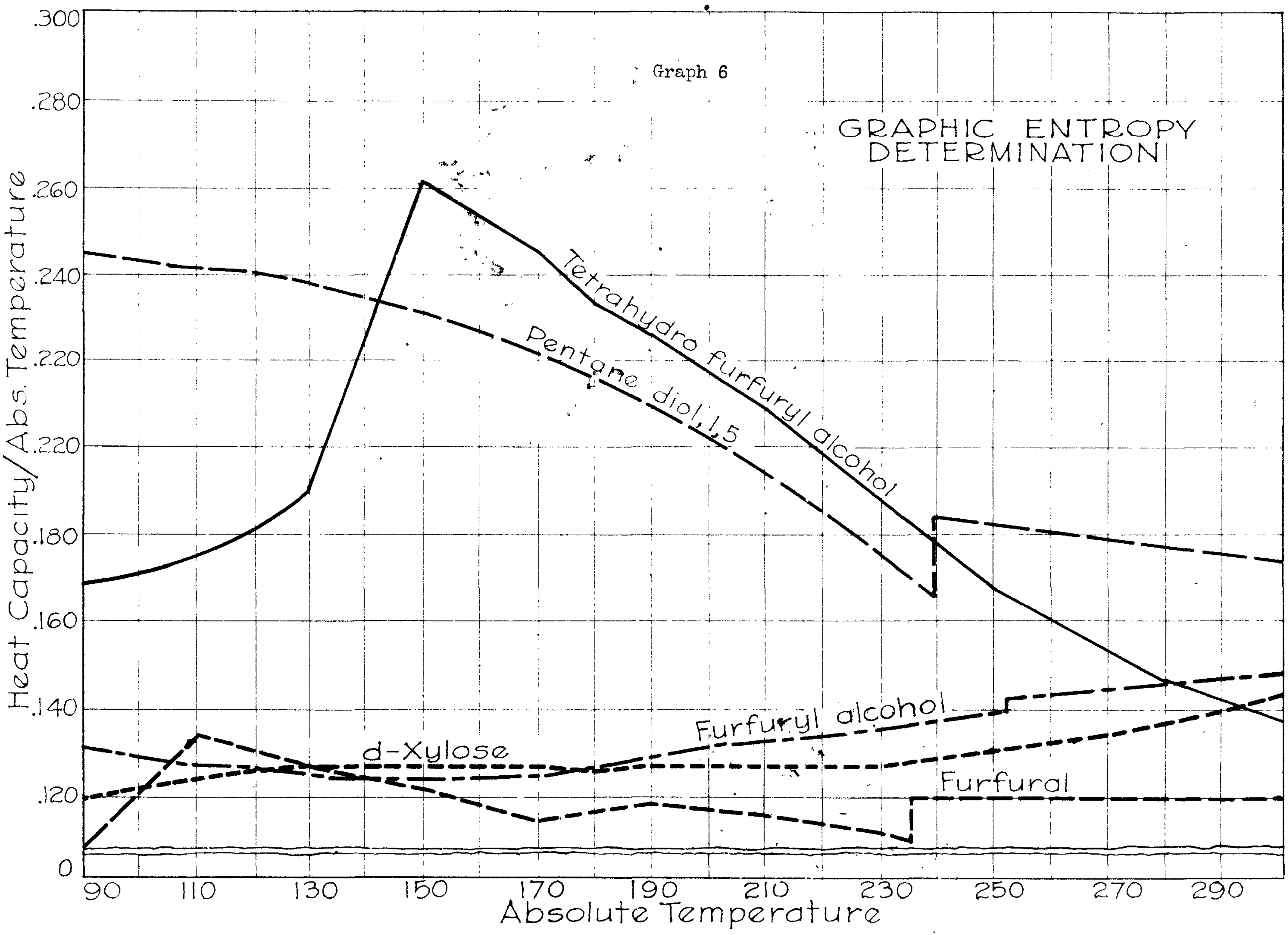

Graph 3
Heat Capacity
Tetrahydrofurfuryl Alcohol
— — — Extrapolated portion of curve
Heat Capacity (Cals/mole/degree
Absolute Temperature
0
5
10
15
20
25
30
35
40
45
50
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
○ CO_2 Run 1
⊗ CO_2 Run 2
● Liquid Air Run 1
⊙ Liquid Air Run 2
× Liquid Air Run 3
⊙ Extrapolated from Kelly, Parks & Huffman's equation.

Graph 4


Heat Capacity of Pentane 1,5 Diol
----Extrapolated portion of curve
Heat Capacity (Cals/mole/degree)
Absolute Temperature
0
5
10
15
20
25
30
35
40
50
55
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
● CO_2 Run 1
○ CO_2 Run 2
△ CO_2 Run 3
× Liquid Air Run 1
◒ Liquid Air Run 2
▣ Liquid Air Run 3
⊙ Extrapolated by using Kelly, Parks & Huffman's equation.

Graph 5


Heat Capacity of d-Xylose
---Extrapolated portion of curve
Heat Capacity (cals/mole/degree)
Absolute Temperature
0
5
10
15
20
25
30
35
40
45
50
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
● CO_2 Run 1
□ CO_2 Run 2
▣ CO_2 Run 3
△ CO_2 Run 4
× Liquid Air Run 1
○ Liquid Air Run 2
⊙ Extrapolated by using Kelly, Parks, & Huffman's equation.


Graph 6

GRAPHIC ENTROPY DETERMINATION
Heat Capacity/Abs. Temperature
.300
.280
.260
.240
.220
.220
.180
.160
.140
.120
0
Absolute Temperature
90
110
130
150
170
190
210
230
250
270
290
Tetrahydro furfuryl alcohol
Pentane diol,1,5
Furfuryl alcohol
d-Xylose
Furfural

The equation for finding entropy $\Delta S_{90} = \Delta S_{90}^{0} + B \int_{0}^{90} Cp^{o}dT$

Where ΔS_{90} = entropy at 90°

ΔS_{90}^{0} = entropy of the standard substance at 90°.

$\int_{0}^{90} Cp^{o}dT$ = the value of which was obtained by Kelly, Parks, and Huffman by graphical integration. A and B are constants.

TABLE XIV

Compound	ΔS Fusion	ΔS 0° to 90°	ΔS 90° to 298.16°	Molal $S_{298.16^{o}}$
Furfural	14.60	12.52	24.98	52.10
Furfuryl alcohol	13.58	10.27	27.65	51.50
Tetrahydrofurfuryl alc.		10.81	41.61	52.42
Pentane 1, 5 diol	15.15	18.76	42.91	76.82
d-xylose		7.50	26.80	34.30

The change in entropy in the formation of a compound was found by subtracting the absolute entropy values for the elements in each compound from the molal entropy.

TABLE XV

Compound	(Molal entropy)	-	(Sum of the absolute entropies)	= ΔS
Furfural	52.10	-	109.55	- 57.45
Furfuryl alcohol	51.50	-	125.16	- 73.66
Tetrahydrofurfuryl alcohol	52.42	-	187.62	-135.20
Pentane 1,5 diol	76.82	-	218.85	-142.03
D-xylose	34.2	-	224.4	-190.1

Calculation of the Free Energy of the Compounds

The equation $\Delta F = \Delta H - T\Delta S$ was used to calculate the free energy of each compound. The data on heat of combustion were taken from Landrieu.(23)(24) The heat of formation was calculated by considering the values for the heat of combustion of carbon to carbon dioxide to be 94.24 Kilogram calories per mole and the value for hydrogen 68.31 Kilogram calories per mole.(34) Table XVI gives the values of members of this equation for each compound.

TABLE XVI

Compound	$\Delta H_{298.16^\circ K}$	$-T\Delta S_{298.16^\circ K}$	$\Delta F_{298.16^\circ K}$
Furfural	- 47,520	+ 15,536	- 31,984
Furfuryl alcohol	- 67,130	+ 21,965	- 45,165
Tetrahydrofurfuryl alc.	-103,250	+ 40,320	- 62,930
Pentane 1, 5 diol	-105,060	+ 42,345	- 62,715
D-xylose	-235,750	+ 57,000	-178,750

Calculations of the Free Energy Change for the Formation of One Mole of Substance at 25° With Hydrogen Present Under a Partial Pressure of One Atmosphere:

The free energy decrease occurring in the formation of furfural from d-xylose is

$$\underset{\text{d-xylose}}{C_5H_{10}O_5} \longrightarrow \underset{\text{Furfural}}{C_5H_4O_2} + \underset{\text{Water}}{3H_2O}$$

ΔF d-xylose = -178,750 cals.   ΔF furfural = - 31,984 cals.
ΔF water (3 moles)= -169,680 cals.(26)
-201,664 cals.

Subtracting the left member from the right member -201,664 cals.
-178,750 cals.
- 22,914 cals.

gives the free energy change for the formation of one mole of furfural from d-xylose.

The free energy change for furfural hydrogenated to furfuryl alcohol is

$$C_4H_3CHO + H_2 \longrightarrow C_4H_3CH_2OH$$

ΔF furfuryl alcohol = -45,165 cals.
ΔF furfural = -31,984 cals.
-13,181 cals.

The free energy decrease from furfural to furfuryl alcohol is 13,181 cals.

The free energy change for hydrogenating furfuryl alcohol to tetrahydrofurfuryl alcohol is $C_4H_3CH_2OH + 2H_2 \longrightarrow C_4H_7CH_2OH$

ΔF tetrahydrofurfuryl alcohol = -62,920 cals.
ΔF furfuryl alcohol = -45,165 cals.
-17,755 cals.

The free energy change for hydrogenating furfuryl alcohol to tetrahydrofurfuryl alcohol is -17,755 cals.

The free energy produced by hydrogenating furfural to pentane 1, 5 diol is $C_5H_4O_2 + \overset{4}{\cancel{3}}H_2 \longrightarrow C_5H_{12}O_2$

furfural   pentane 1, 5 diol

ΔF pentane diol = -63,715 cals.
ΔF furfural = -31,984 cals.
The free energy change is -31,731 cals.

DISCUSSION

Factors Affecting Accuracy

Heat of Combustion

The factors affecting accuracy were measurement of the temperature change, stirring of the calorimetric liquid and heat transfer between the calorimeter and jacket. These were minimized by running the determinations in exactly the same manner as the standardization. The weight of water used in a determination, which was known to about a gram, would cause an error of less than one part in two thousand.

The Beckmann thermometer was graduated in hundredths of a degree and the temperature was read to three decimal places by estimating the last figure. Parallax was eliminated by using a special thermometer lens. The thermometer was tapped before each reading to prevent sticking of the mercury. The error in reading the thermometer was about 0.002°. When the change in temperature was 2.5°, this would be an error of one part in 1250. The open bucket makes evaporation and splashing an uncertain factor. The water equivalent of the bomb was found to be the same as the manufacturer's equivalent. Brodie and Jennings(5) found a higher value, calories (470), but the bomb contained additional equipment when they were using it.

The value for the heat of combustion of pentane 1, 5 diol was 752.3 Kilogram calories. A check by calculating the heat of combustion of this compound by the method proposed by Kharasch is interesting.(18) The value calculated by his method was 755 Kilogram calories which is in fair agreement considering the approximate nature of Kharasch's method. The heat of combustion of furfural was found to be 558.3 Kilogram calories per mole. The value found by Landrieu was 559.8 Kilogram calories.(18)

Heat Capacity

Heat may leak into or out of the apparatus in three ways. First, the leak through the wires and silk thread. This was accounted for in the calibration of the apparatus. Second, the effect of radiation which was eliminated in the same manner, at low temperatures it is low and is minimized by having all surfaces bright and shining. Third, conduction by the gas. The effect of gas pressure on heat conductivity is more important than is commonly supposed. Knudsen(19) has shown that at low pressures conductivity is directly proportional to the pressure of the gas. The pressure was kept at 0.1 micron or lower. No difference in the heat capacity could be observed in the calculations when the pressure was 0.1 micron or lower.

The thermoelement loses sensitivity at low temperatures as the electromotive force per degree becomes less. The readings at low temperature were, therefore, not quite as accurate as the readings above the sublimation point of solid carbon dioxide.

If a determination of heat capacity lasted only one minute, an error of one second caused an error of one part in sixty. For this reason the time of a determination was usually from four to seven minutes. The time was measured by using the second hand on an electric clock. The time error was due to failures in starting and stopping the current exactly on time and taking the thermoelement reading exactly on the second. The error was usually not over 0.2 second as the potentiometer dial was kept moving with the changing potential and the motion stopped as the second hand passed the minute mark. The current switch was kept just above the point of making contact and then closed at the proper instant.

The voltage drop was measured by the potentiometric method, and could be kept constant to within 0.01 volt as a very small part of one volt produced a galvanometer deflection and adjusting the micrometer resistance was the limiting factor. The resistance of the heating coil was measured to one part in a thousand by means of a wheatstone bridge and the effect of the change in resistance at lower temperature was minimized by the calibration.

The potential created by the thermoelement is about 15 microvolts per degree at liquid air temperature and about 40 microvolts per degree at room temperature. The sensitivity of the galvanometer is 1.5 microvolts. The sensitivity is then about 0.1° at the lower temperatures and 0.04° at the higher temperatures.

CONCLUSIONS

The formation of furfural from d-xylose is a spontaneous process, being attended with a free energy decrease of 22,914 calories.

The standard free energy of the hydrogenation of furfural to furfuryl alcohol is attended by a decrease of 13,181 calories.

The standard free energy of the hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol is attended by a free energy decrease of 17,755 calories.

The standard free energy of the hydrogenation of furfural to pentane 1, 5 diol was found to involve a decrease of 31,731 calories.

The standard free energy is found in the conclusions by assuming the formation of one mole of substance at 25°, the hydrogen gas being present at a partial pressure of one atmosphere. The free energy of hydrogen is arbitrarily taken at zero.

SUMMARY

1. The heat of combustion of pentane 1, 5 diol has been determined.
2. The heat capacity from 100 to 298.16 K has been found for: furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, pentane 1, 5 diol, and d-xylose.
3. The heat of fusion has been determined for: furfural, furfuryl alcohol, and pentane 1, 5 diol.
4. The entropies at 298.16K have been determined for furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, pentane 1,5 diol, and d-xylose.
5. The free energies at 298.16K of: furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol and d-xylose have been determined.
6. The free energies of the furfural hydrogenation products decrease as hydrogen is added to the molecule.
7. When d-xylose forms furfural there is a free energy decrease.

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