[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LELAND STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS

I. THE HEAT CAPACITIES AND FREE ENERGIES OF METHYL, ETHYL AND NORMAL-BUTYL ALCOHOLS

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If adequate heat-capacity data exist for a given compound and for the elements contained in it, the entropy of formation of the substance for a given temperature —ΔS— can be calculated by means of the third law of thermodynamics.[1] If then ΔH, the heat of formation, is also known, the free energy of formation of the compound, ΔF, can be obtained by use of the thermodynamic relationship

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

Thus there is now available a very powerful instrument for the determination of the free energies of organic substances. It is the author's plan to utilize this method in building up a free-energy table for the simpler aliphatic compounds.

The present paper presents some heat-capacity data on methyl, ethyl and *n*-butyl alcohols and their free energies calculated therefrom.

Experimental Part

Method.—The method was essentially similar to that described by Gibson, Latimer and Parks,[2] although their apparatus was modified in a number of details in order to obtain greater accuracy. Several of these modifications were substantially those adopted by Rodebush[3] in his work on cadmium and tin.

The alcohol sample was contained in a gas-tight, cylindrical copper can, 8 cm. long and 2.5 cm. in diameter, with a capacity of approximately 40 cc. To facilitate the attainment of thermal equilibrium the inside of this container was fitted with more than 40 perforated disks, spaced about 2 mm. apart along a small copper tube which ran through the center of the cylinder and served as a holder for the thermocouple used in measuring temperatures. These disks, even though made out of extremely thin copper foil, added considerably to the weight of the calorimeter; their use, however, was justified by the fact that in this way no portion of the liquid under investigation could be more than 1 mm. from a highly conducting copper surface. A 120-ohm heating-coil made from B. and S. No. 36, silk-insulated Therlo wire was wound around the outer surface of the can and baked on with electricians' enameling fluid; it had external leads of No. 40

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[1] Lewis and Gibson, THIS JOURNAL, **42,** 1533 (1920).

[2] Gibson, Latimer and Parks, *ibid.*, **42,** 1504 (1920).

[3] Rodebush, *ibid.*, **45,** 1413 (1923).

copper wire. To reduce heat losses through radiation and to provide a uniform, unoxidizable surface, thin platinum foil was then wrapped tightly around the container. A short entry tube 1.6 mm. in diameter, which could be sealed with soft solder, provided a means of filling and emptying the can. Two different calorimeters constructed with these features weighed 30 and 43 g., respectively. Their heat capacities in the unfilled state, representing from 15 to 20% of the total heat input during a specific-heat determination on the alcohols, were measured in a separate series of experimental runs.

The calorimeter was suspended by silk thread within a larger copper cylinder weighing about 600 g. This sheath, fitted with a top and bottom and silvered on both its inner and outer surfaces, provided a relatively uniform temperature environment for the specific-heat determinations. In order to control its temperature it was equipped with a heating-coil and thermocouple. The cylinder and contents rested on small wooden legs in a vacuum-tight brass can, 5 cm. in diameter and 15 cm. long. A german-silver tube 1 cm. in diameter and 50 cm. long, soldered into a hole in the top of the brass can, served the three-fold purpose of connecting the system to the evacuating apparatus, of providing an exit path for the electrical connections and of serving as a support, the entire apparatus being suspended in a 1000-cc. Dewar jar. Details of electrical wiring, bringing out the connections, evacuating the system, etc., were essentially similar to those described by Rodebush.

During a specific-heat determination heat was supplied to the calorimeter by means of an electric current from an 8-volt battery. The energy input was measured with an accuracy of 0.1% by a calibrated stop watch and a potentiometric evaluation of the current and voltage. In general it was such as to cause a temperature rise of about 4°.

Single-element copper-constantan thermocouples, constructed from B. and S. No. 40 silk-insulated copper and No. 30 silk-insulated constantan wire were used with a White potentiometer in measuring the temperatures involved. For these thermocouples the temperatures and the rates of change of e.m.f. with change of temperature, dE/dT, were obtained by use of the two equations of Eastman and Rodebush,[4] since the wire that I used had been given to me by Professor Latimer and was evidently similar to theirs. More recently, a single equation valid for the copper-constantan element over the entire range of temperatures from that of liquid air to 0° has been suggested by Adams.[5] However, as some calculations made for purposes of comparison indicated that the two sets of values for dE/dT, obtained, respectively, from the equations of Eastman

[4] Eastman and Rodebush, THIS JOURNAL, **40**, 492 (1918).

[5] Adams, "Pyrometry," Am. Inst. Min. Metallurg. Engineers, New York, **1920**, p. 170.

and Rodebush and from that of Adams in conjunction with the slope of a deviation curve, differed on the average by only 0.1% above 200° A. and by about 0.33% below this point, there seems to be little choice as far as accuracy is concerned. In the present case Adams' equation would have involved much larger deviation corrections and hence was less convenient. Probably the Eastman-Rodebush values for dE/dT are accurate to within 0.2% or better above 200° A.; below this point the accuracy may fall in some places to about 0.5%.

The actual procedure in making the measurements and in calculating, therefrom, the specific-heat values was essentially as described in the previous paper[2] and need not be repeated here. As a conversion factor for changing joules to 15° calories the value 0.2391 was used throughout.

Purification of Materials

Methyl Alcohol.—The methyl alcohol was a very pure sample of "reagent quality" obtained from the Mallinckrodt Chemical Works. Further distillation over calcium oxide and metallic sodium produced no appreciable decrease in its specific gravity; d_4^{22}, 0.7892. Its melting point during the determination of the heat of fusion was very sharp, indicating a high degree of purity.

Ethyl Alcohol.—Two different samples of ethyl alcohol were used for the two sets of measurements. Sample A was prepared from a good grade of "absolute" alcohol by distillations over lime and over metallic calcium, respectively. The product thus obtained was carefully fractionated and the middle portion, about one-half of the total, was used for the first set of measurements on ethyl alcohol. It had a density corresponding to 99.98% ethyl alcohol according to the tables of the United States Bureau of Standards.[6] Sample B was from a material prepared for another investigation by Mr. Kenneth Kelley. According to his density determination it was 99.97% ethyl alcohol. This liquid was allowed to stand over lime for several weeks and was then distilled and fractionated; the middle portion was used for the second set of measurements on ethyl alcohol.

Butyl Alcohol.—The *n*-butyl alcohol was prepared from a "refined" commercial product; b. p., 116–118°. This was distilled over a small amount of metallic calcium and then twice fractionated carefully. The final sample, amounting to less than 20% of the total, had a boiling range of 0.1°. This was probably the least pure of the materials used, although its melting point was reasonably sharp.

Specific Heats

The results for the specific heats of the alcohols studied appear in Table I. In the case of the methyl and *n*-butyl alcohols every experimental determination is given.

In the case of crystalline and liquid ethyl alcohol a far greater number of determinations were made, some of them being preliminary in character, and it hardly seems desirable to present the entire mass of data here. The measurements on Samples A and B were made two years apart, with different calorimeters, different thermocouples, etc. The results for Sample A averaged somewhat lower than those for B—about 0.2% in the

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[6] *Bur. Standards Sci. Paper*, 197 (1913).

liquid state and 0.5% in the crystalline. In view of these facts, the most probable curve was drawn and the values read from it at even temperatures. These are the figures for ethyl alcohol presented in Table I; without doubt they are more reliable than the data in the earlier paper.[7]

Methyl alcohol was found to have two crystalline forms with a transition point at 161.1°K. As the second form melts at 175.3°K. it is stable over an interval of less than 15° and its specific heat was not measured separately. Instead the heat of transition and the specific heat of this second form were determined together with the heat of fusion, data for which are presented in the following section of this paper.

In general, it is believed that the results are accurate to within 0.5% above 200°K.; below this point the accuracy, on account of systematic errors in the temperature scale, etc., may fall to 99%. In the case of the supercooled or glass form of ethyl alcohol the errors may be considerably larger than this value in the region of rapid increase of the heat capacity, owing to uncertainty in the attainment of thermal equilibrium as well as to the

Table I

Specific Heats

All weights reduced to a vacuum basis

Methyl Alcohol

Crystals I

Temp., °K.	88.7	91.3	93.4	97.3	101.2	106.8	106.9	112.2	144.7	151.9
C_p per g	0.304	0.310	0.314	0.324	0.331	0.345	0.344	0.357	0.419	0.441

Liquid

Temp., °K.	188.4	193.5	197.1	225.9	274.9	276.0	285.7	290.1
C_p per g	0.527	0.529	0.530	0.535	0.576	0.578	0.590	0.597

Ethyl Alcohol

Crystals

Temp., °K.	87.0	90.0	95.0	100.0	110.0	120.0	130.0	140.0
C_p per g	0.231	0.236	0.244	0.251	0.266	0.281	0.296	0.312

Liquid

Temp., °K.	160.0	200.0	240.0	250.0	275.0	290.0	298.0
C_p per g	0.455	0.468	0.496	0.507	0.543	0.572	0.588

Glass

Temp., °K.	86.8	87.5	88.1	90.8	91.9	95.8	97.5	100.5	105.5	110.2
C_p per g	0.264	0.266	0.263	0.296	0.301	0.420	0.443	0.423	0.399	0.415

n-Butyl Alcohol

Crystals

Temp., °K.	90.6	90.8	98.4	99.9	104.7	111.0	144.8	151.3
C_p per g	0.195	0.196	0.207	0.209	0.215	0.225	0.267	0.276

Liquid

Temp., °K.	194.6	197.5	198.3	224.5	254.9	274.8
C_p per g	0.442	0.444	0.444	0.463	0.494	0.524
Temp., °K.	275.1	275.1	275.6	276.6	290.4	294.0
C_p per g	0.527	0.525	0.527	0.526	0.560	0.565

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[7] Ref. 2, p. 42, 1542.

incipient crystallization which made measurements above 115°K. impossible. In this region some of the individual determinations are possibly in error by 4 or 5%.

Heats of Fusion

The same apparatus was used in determining the heat of fusion and melting point of each alcohol. In these measurements the rate of input of energy was increased by using batteries of 12 or 16 volts. The heating current was turned on when the calorimeter and contents were 8° to 20° below the melting point and continued until a temperature +1° to +5° had been reached. In the calculation of the heat input for the fusion process the specific-heat values for the alcohol in the crystalline and liquid state were obtained by extrapolation of the curves for the experimental values in Table I. The results for the heat of fusion are probably accurate to within 1%. In the case of the heat of transition between the two solid forms of methyl alcohol and the specific heat of Crystals II, the error may be greater—possibly 2 or 3%.

Table II

Heats of Fusion

All weights reduced to a vacuum basis

Substance	Melting point °K.	Heat of fusion (cal. per g.)
Methyl alcohol	175.3	23.7
Ethyl alcohol	158.7	25.55 (Sample A)
		25.78 (Sample A)
		26.05 (Sample A)
		25.73 (Sample B)
	Weighted mean	25.76
n-Butyl alcohol	183.9	29.88
		29.98
	Mean	29.93

Heat of transition of methyl alcohol at 161.1°—4.4 cal. per g.
Specific heat of crystals II, methyl alcohol, at 168.3°—0.40 cal. per g.

Discussion

Entropies of the Alcohols.—Assuming the entropy at absolute zero to be zero, the entropy S of a substance at 298°K. (or 25°C.) is given by the equation

$$S_{298} = \int_0^{298} \frac{dQ}{T} \tag{2}$$

More specifically for ethyl alcohol,

$$S_{298} = \int^{90} \frac{C_p(\text{crystals})}{T}\, dT + \int_{90}^{158.7} \frac{C_p(\text{crystals})}{T}\, dT + \frac{\Delta H(\text{fusion})}{158.7} + \int_{158.7}^{298} \frac{C_p(\text{liquid})}{T}\, dT \tag{3}$$

The first integral in this expression, $\int_0^{90} \frac{C_p(\text{crystals})}{T}\, dT$, cannot be evaluated directly from the experimental data, since the specific heats do not go much below 90°. Some method of extrapolation is, therefore, necessary and in the present case the "n formula" of Lewis and Gibson[8] has been utilized. By application of their methods to the data for crystalline ethyl alcohol, the values $n = 0.305$, $\log \Theta = 2.726$ and $S_{90} = 13.19$ entropy units per mole have been obtained. To what extent this result, 13.19, may be in error it is very hard to say. Possibly the absolute error may be of the order of 1 entropy unit, but for the purposes of a comparative study of the entropies of the three alcohols the value will be retained as given above, since in all probability the application of the Lewis-Gibson extrapolation method to several similar substances involves comparable errors.

The remaining three terms on the right-hand side of Equation 3 can be evaluated, with much greater certainty. The quantity $\Delta H(\text{fusion})/158.7$ is obtainable directly from the experimental data of Table II. The two integrals were determined graphically by plotting the values of C_p per mole as ordinates against lnT as abscissas and measuring the area under the curve. The results appear in Table III and are accurate to within 1% or better.

In a similar way the entropies of methyl and *n*-butyl alcohol were determined, the results also appearing in Table III. In the case of methyl alcohol $n = 0.388$ and $\log \Theta = 2.396$; for *n*-butyl alcohol, $n = 0.298$ and $\log \Theta = 2.887$.

TABLE III

ENTROPIES OF THE ALCOHOLS PER MOLE

	CH_3OH	C_2H_5OH	C_4H_9OH
Crystals I (0–90°K.)	9.74	13.19	17.64
Crystals I, above 90°K	7.26	7.38	13.25
Transition	.87	...	...
Crystals II	1.06	...	...
Fusion	4.33	7.47	12.07
Liquid	9.30	14.28	17.24
$S_{298°}$	32.6	42.3	60.2

The increase in the value of S_{298} in going from CH_3OH to C_2H_5OH is 9.7 units; in going from the latter to C_4H_9OH it is 17.9, or roughly twice the first increase. Possibly there may be a general relationship between entropy magnitudes and chemical constitution such that the introduction of a CH_2 group corresponds to a definite increase in entropy. It is hoped that an investigation now under way in this Laboratory will throw further light on the question.

Richards and Davis[9] have made a very careful study of the heats of

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[8] Lewis and Gibson, THIS JOURNAL, **39**, 2565 (1917).

[9] Richards and Davis, *ibid.*, **42**, 1614 (1920).

combustion at constant volume of a number of organic compounds. Weighing in air and using the 18° calorie, they obtained for these three alcohols 170,830 cal., 327,450 cal. and 639,140 cal., respectively. From these values the heats of combustion at constant pressure and 298°K. have been calculated in terms of the 15° calorie;[10] the results appear in Col. 2 of Table IV. In the third column are the corresponding figures for ΔH, the increase in heat content during formation of the alcohols from their elements. These were obtained from the heats of combustion at constant pressure by the use of the respective values —94,250 cal. and —68,270 cal. for the ΔH of formation of carbon dioxide and water from their elements.[11] Next in the table are the entropy changes, ΔS, for the process of producing the several alcohols from their elements. They are simply the differences between the entropies of the compounds in Table III and the entropies of their elements as calculated by Lewis, Gibson and Latimer.[12]

TABLE IV

THERMAL DATA

The 15° calorie is used throughout

Alcohol	Heat of combustion at constant pressure cal.	ΔH_{298} cal.	ΔS_{298} entropy units	ΔF_{298} cal.
CH_3OH	170,900	−59,890	− 51.6	−44,500
C_2H_5OH	327,650	−65,660	− 72.6	−44,000
C_4H_9OH	639,580	−78,770	−116.2	−44,100

In the last column appear the free energies of the respective alcohols, calculated by use of Equation 1. The three results average 44,200 cal. and differ from one another by less than the probable experimental error. This fact indicates that the addition of a CH_2 group in an aliphatic series causes no appreciable change in free energy. The heat content does decrease and also the entropy of formation, but these changes are apparently parallel and neutralize each other.

The Entropy Difference between the Two Forms of Ethyl Alcohol

In the earlier paper of Gibson, Parks and Latimer, a comparison was made between the entropies of ethyl alcohol in the crystalline and glassy forms. From their rather scanty data, it appeared that the glass exceeded the crystals by 2.52 entropy units per mole at 78°K. and it seemed hardly probable that this entropy difference would become zero at the absolute zero. The data of the present paper are unquestionably more reliable and afford a basis for a recalculation of this difference.

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[10] The conversion from the 18° calorie to the 15° calorie was made by division by the factor 1.0007.

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 477, 571.

[12] Lewis, Gibson and Latimer, THIS JOURNAL, **44,** 1008 (1922).

The excess entropy of the glass over the crystals at 87°K., $\Delta S_{87°}$, is given by the equation

$$\Delta S_{87} = \frac{\Delta H(\text{fusion})}{158.7} - \int_{87}^{158.7} \frac{C_p,\text{ glass} - C_p,\text{ crystals}}{T}\,dT \qquad (4)$$

and was found to equal 3.71 entropy unit per mole. At 87° the entropy of the crystals, calculated with the aid of the Lewis-Gibson "*n* formula," is 12.82 units per mole and the specific heat of the glass is 14% greater than that of the crystalline form. If this same excess in heat capacity continues to the lowest temperatures,[13] the decrease in entropy of the glass from 87° to 0°K. would be greater than the corresponding decrease for the crystals by 1.92 unit per mole. In this case, the entropy of the glass at zero absolute would exceed that of the crystals by 1.79 unit per mole. By the same line of reasoning the earlier data indicated an excess of a 1.08 unit.

Summary

1. The specific heats of crystalline and liquid methyl, ethyl and *n*-butyl alcohol have been determined over a wide range of temperature. Some data on the heat capacity of the super-cooled or glassy form of ethyl alcohol have also been obtained.

2. The heat of transition of methyl alcohol and the heats of fusion of all three substances have been measured.

3. The entropies and free energies of these alcohols have been calculated. Corresponding to each additional CH_2 group there is an average entropy increase of 9.2 units but no change in the molal free energy.

4. The entropy of glassy ethyl alcohol has been found to exceed that of the crystalline form by 3.7 units per mole at 87°K. It seems improbable that this difference becomes zero at the absolute zero.

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[13] The assumption that the heat capacity of the glass exceeds that of the crystals by 14% at all temperatures from 87°K. to the absolute zero is highly improbable. It has been used as a basis for calculation in the present case simply because the author desires to be conservative in his estimate of the entropy excess of the glass over the crystals. The data of Gibson and Giauque [This Journal, **45,** 94 (1923)] for crystalline and glassy glycerol show that, as relatively lower temperatures are attained, the heat-capacity curves for the two substances approach to within 1 or 2% of each other. Their results indicate in an even more convincing manner that there is an entropy difference between a glass and the corresponding crystals at 0°K.