area). The thicknesses of the water films on salt solutions correspond to 7.5 Å. of area for the thickest and 13 for the thinnest films. The square roots of these areas are 2.7 and 3.6 Å. of length. These dimensions indicate that the departure of the molecule from exact symmetry would not need to be very great in order to account wholly for the change in the thickness of the film. It seems probable, however, that other factors are also effective.

2. Accurate measurements have been made of the surface tensions of sodium chloride solutions from 0.1 to 5 *M*.

3. The adsorption isotherm of Gibbs has been put in a form by means of which the adsorption of either an organic substance or a salt may be calculated. Earlier forms of this equation take no account of the activity coefficient of the salt, which falls to a minimum at about 1 *M* with a value of 0.65. At a molality of 5.54 this has increased to 0.874 and this large increase indicates that calculations of adsorption which neglect this coefficient are highly in error. In the most dilute solution used in the present work one positive and one negative ion are present to 555 molecules of water; in the most concentrated, one ion of each charge to 10 molecules of water. The characteristics and charge of both the positive and negative ions are of influence upon the surface tension. In the surface the layer of water on a hydrated ion seems to be not more than one molecule of water thick, but the possibility that some of these molecules may be of the type $(H_2O)_2$ is not entirely excluded.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. II. THE HEAT CAPACITIES OF FIVE ORGANIC COMPOUNDS. THE ENTROPIES AND FREE ENERGIES OF SOME HOMOLOGOUS SERIES OF ALIPHATIC COMPOUNDS

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In an earlier article,[1] the entropies and free energies of three primary alcohols, methyl, ethyl and *n*-butyl, were calculated from heat-capacity data by means of the third law of thermodynamics. The free-energy values thus obtained were identical within the limits of experimental error and averaged —44,200 calories. Thus it appeared that in this series of primary alcohols the introduction of an additional CH_2 group was without appreciable effect on the free energy of the alcohol, and the question at once arose as to whether regularities also exist in other homologous series. To answer this question partially the heat capacities of five other organic

[1] Parks, THIS JOURNAL, **47**, 338 (1925).

compounds, namely, *iso*propyl alcohol, acetone, ethylene glycol, acetic acid and palmitic acid, have been measured between the temperature of the room and that of liquid air. These results, when combined with the data of several other investigators, indicate quite clearly that there is a definite correspondence between the constitution of an organic compound and its entropy and free energy.

Experimental Part

Method.—The apparatus and details of experimental procedure were essentially the same as those described in the first article of this series. In view of the accuracy of the various measurements involved, we believe that the error in the specific heats and heats of fusion thus obtained is less than 1%, except in so far as impurities in the materials used may influence the results.

Materials

***iso*Propyl Alcohol.**—"Refined" *iso*propyl alcohol was first dehydrated by two successive distillations over lime in the ordinary manner. The resulting product was carefully fractionated and the middle portion, about 60% of the total, was selected for use in the present investigation. It had a density of 0.78086 at 25°/4°, which corresponds to 99.99% alcohol on the basis of Brunel's value[2] of 0.78084 for 100% and the variation per 1% of water of 0.00230 obtained by Lebo.[3] To this material a small amount of lime was again added and in each case the alcohol was distilled therefrom just before use. Two samples were studied in the present investigation with different lead-wire connections, thermocouple thermometers, etc. The results of the two sets of determinations, made over a year apart, agreed to 0.5% or better and served to indicate the reproducibility of the values obtained.

Acetone.—Pure, absolute acetone, obtained from the National Aniline and Chemical Company, was used without further purification.

Ethylene Glycol.—The source of the ethylene glycol was a C. P. product. This was carefully fractionated and the middle portion, which represented about a third of the total and had a boiling range of 0.15°, was used for the measurements. Unfortunately, its high viscosity rendered the operation of filling the calorimeter difficult and led to rather long exposure to the air during this procedure. An estimate of its purity, made in connection with the heat of fusion determinations, gave about 99 mole per cent. This value corresponds to 99.7% ethylene glycol on the assumption that water is the sole impurity.

Acetic Acid.—A high grade material (99.9% acetic acid, m. p. 16.6°) was subjected to two fractional crystallizations before use in the measurements.

Palmitic Acid.—The palmitic acid investigated was an Eastman product; m. p., 61.7°. It was comparatively free from inorganic impurities, as a sample on ignition gave only 0.02% of residue.

Specific Heats

The experimental values for the specific heats of the various substances appear in Table I. They are expressed in terms of the 15° calorie and with all weights reduced to a vacuum basis.

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[2] Brunel, THIS JOURNAL, **45**, 1336 (1923).

[3] Lebo, *ibid.*, **43**, 1006 (1921).

In each case the heat capacity was found to rise very noticeably on approaching the melting point. This effect, while it may be largely due to

TABLE I

SPECIFIC HEATS

*iso*PROPYL ALCOHOL

Crystals

Temp., °K.	70.7	76.6	82.7	88.5	92.2	93.0	95.5
C_p per g.	0.173	0.183	0.193	0.202	0.208	0.209	0.213

Temp., °K.	99.7	101.3	106.5	111.6	152.5	153.2
C_p per g.	0.220	0.221	0.228	0.236	0.308	0.309

Liquid

Temp., °K.	195.4	198.5	199.1	227.0	275.3	284.0	287.6	290.2	293.1
C_p per g.	0.443	0.446	0.447	0.472	0.556	0.579	0.585	0.595	0.606

ACETONE

Crystals

Temp., °K.	69.6	74.2	79.7	85.6	90.8	91.2
C_p per g.	0.219	0.229	0.239	0.250	0.257	0.259

Temp., °K.	95.2	100.1	104.3	105.3	151.2	153.0
C_p per g.	0.266	0.272	0.278	0.281	0.350	0.352

Liquid

Temp., °K.	193.2	196.6	200.1	210.3	217.5	276.9	279.3	283.4	286.4	289.4
C_p per g.	0.480	0.480	0.482	0.485	0.485	0.507	0.508	0.509	0.513	0.513

ETHYLENE GLYCOL

Crystals

Temp., °K.	88.4	89.1	90.6	90.8	107.8	154.5	193.3
C_p per g.	0.163	0.163	0.165	0.166	0.186	0.236	0.277

Temp., °K.	195.1	196.8	198.4	209.6	214.0	227.2
C_p per g.	0.279	0.282	0.283	0.301	0.309	0.334

Liquid

Temp., °K.	262.0	263.2	275.6	278.2	288.0	293.0
C_p per g.	0.537	0.538	0.552	0.556	0.571	0.575

ACETIC ACID

Crystals

Temp., °K.	87.4	89.1	90.4	90.7	94.7	95.5	96.1	100.0
C_p per g.	0.187	0.189	0.190	0.192	0.195	0.197	0.197	0.200

Temp., °K.	153.5	194.6	197.7	198.9	232.5	238.9	255.5	274.7
C_p per g.	0.239	0.262	0.266	0.268	0.288	0.296	0.311	0.351

Liquid

Temp., °K.	292.6	294.7
C_p per g.	0.488	0.491

PALMITIC ACID

Crystals only

Temp., °K.	88.4	93.7	97.4	102.3	107.1	110.2	111.7	151.9	160.8
C_p per g.	0.160	0.167	0.171	0.177	0.182	0.186	0.186	0.229	0.237

Temp., °K.	193.5	197.6	215.4	234.5	237.9	274.9	275.3	289.4	292.5
C_p per g.	0.271	0.275	0.295	0.320	0.324	0.383	0.384	0.417	0.431

impurities which cause a small amount of premature melting, is certainly a very general phenomenon.

Fusion Data

The melting points and heats of fusion of *iso*propyl alcohol, acetone, ethylene glycol and acetic acid were also determined, the results appearing in Table II. In the calculation of these fusion values, the marked rise in the specific heat of the solid as the melting point is approached was attributed to premelting, and the heat absorbed in this region in excess of that obtained by extrapolation of the specific-heat data at lower temperatures was added to the heat absorbed at the melting point. This procedure, while it may not be entirely justifiable, can certainly lead to no appreciable error in the calculation of the entropies in the following section of this paper. On the other hand, it is noteworthy that in the case of acetic acid the values for the heats of fusion which we have thus obtained are higher by 0.8 and 1.6%, respectively, than the apparently accurate results of de Visser and Meyer.[4]

TABLE II

FUSION DATA

Substance	Melting point °K.	Heat of fusion (Cal. per g.) 1st result	2nd result	Mean
*iso*Propyl alcohol	184.6	21.03	21.14	21.08
Acetone	177.6	23.47	23.37	23.42
Ethylene glycol	260.8	44.68	44.84	44.76
Acetic acid	289.8	46.75	46.61	46.68

Discussion

Entropies of the Compounds.—Using the data contained in Tables I and II together with those of Gibson and Giauque[5] for glycerol, Nernst's specific heats[6] for oxalic acid and Simon's[7] results on glucose, we have calculated the entropy of each of these eight compounds at 298.1° K. In these calculations we have employed the "*n* formula" of Lewis and Gibson[8] for obtaining the entropy increases for the crystals, Col. 2 of Table III, from zero absolute to 90° K. The entropy increments of the crystals from 90° K. to the melting point, or to 298° K. in the three cases where the substance melts above room temperature, were obtained by plotting the heat capacities per mole against the corresponding values for $\ln T$ and integrating the expression, $C_p d \ln T$, graphically. Col. 4 of the table contains the entropy of fusion of each compound, which is simply the molecular

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[4] Landolt-Börnstein-Roth-Scheele, "Tabellen," Julius Springer, Berlin, 1923, p. 1472.

[5] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

[6] Nernst, *Ann. Physik*, **36**, 416 (1911).

[7] Simon, *ibid.*, **68**, 258 (1922).

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

heat of fusion divided by the absolute temperature of the melting point. In the fifth column we have the increases for the liquids from the melting point to 298° K., again obtained by graphical integration. The resulting values for the total entropy appear under the heading S_{298} in the last column.

TABLE III

ENTROPIES OF THE SUBSTANCES PER MOLE

	Crystals				
Substance	0–90° K.	Above 90° K.	Fusion	Liquid	S_{298}
*iso*Propyl alcohol	12.72	11.75	6.86	14.30	45.6
Acetone	17.12	12.50	7.65	14.78	52.0
Glycol	11.46	16.12	10.66	4.61	42.9
Glycerol	13.36	23.57	15.02	1.23	53.2
Acetic acid	18.36	17.50	9.66	0.82	46.3
Palmitic acid	51.20	78.66	..	..	129.9
Oxalic acid	10.90	19.50	..	..	30.4
Glucose	15.86	37.54	..	..	53.4

In the preceding study of the heat capacities of primary aliphatic alcohols, one of us found an average entropy increase for the CH_2 increment of 9.2 cal. per degree in going from methyl to *n*-butyl alcohol. We may now make a similar comparison in the acid series. To do this, however, we should have the entropy of liquid rather than solid palmitic acid at 298° K. In a very accurate determination of the heat of fusion of palmitic acid, Stratton and Partington[9] have recently obtained a value of 13,070 cal. per mole at the melting point 62.6° C. The corresponding entropy of fusion is 38.9 cal. per degree. On the assumption of an average specific heat of 0.50 cal. per g. for the liquid and 0.45 cal. per g. for the crystals, the entropy of fusion at 298° K. is 1.5 less than this or 37.4 units per mole. S_{298} for the acid in the liquid state then equals 130 + 37 or 167 cal. per degree. Taking the entropy of formic acid as 34.2,[10] we find, therefore, an increase of 12.1 units in going from formic to acetic acid and an average increase of 121/14 or 8.6 units per CH_2 group in going from acetic to palmitic acid. Thus, in view of the present data and also those relating to the primary alcohols previously studied, it seems reasonable to conclude that in an homologous series of liquids there is an average entropy increment of 9 ± 1 for each additional CH_2 group. On this basis the value 34.2 for formic acid must be considered irregular but this exception is in no way surprising, as in general formic acid differs very noticeably from the other members of the fatty acid series.

In the series consisting of methyl alcohol, ethylene glycol and glycerol the corresponding entropies are 32.6, 42.9 and 53.2 cal. per degree. Thus we have a difference of 10.3 entropy units for each additional CH(OH)

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[9] Stratton and Partington, *Phil. Mag.*, **48**, 1089 (1924).

[10] Gibson, Latimer and Parks, THIS JOURNAL, **42**, 1540 (1920).

group when we consider the compounds in the liquid state. However, as the higher members of this series are crystalline at room temperature, it is perhaps more instructive to make entropy comparisons for the compounds in the solid state. Accordingly, we have also calculated S_{298} for crystalline glycol and glycerol by extrapolating the heat-capacity curves for the crystals in each instance to 298° K.[11] The respective results are 30.7 and 37.7, and the increase per CH(OH) increment is thus 7 units for the solid state. On this basis the entropy per mole of mannitol at 298° K. might be predicted to be $37.7 + 3(7.0)$, or 58.7 cal. per degree; while Linhart,[12] from very scanty specific-heat data, has calculated 56.8 for the same substance, and the entropy of glucose, which contains two less hydrogen atoms, has just been found to be 53.4 cal. per degree. The difference of 1.9 units between Linhart's result and our estimate is well within the error of his calculation and, even if real, indicates that our predicted value will cause an error of less than 600 cal. in obtaining the free energy of mannitol by the third law of thermodynamics.

Another type of entropy regularity is found when we consider an organic acid to be derived by oxidation from the corresponding alcohol; thus acetic and oxalic acids might be viewed as the oxidation products of ethyl alcohol and ethylene glycol, respectively. Again in the present case, we should make all comparisons with the acids in the same condition and, as we have data for oxalic acid in the crystalline state only, we have also calculated S_{298} for crystalline formic and acetic acids. The results are contained in Table IV and indicate that for the process, $—CH_2(OH)$, liquid $\longrightarrow$ $—CO_2H$, solid, there is an entropy decrease during oxidation averaging 6.4 units.

TABLE IV

ENTROPY CHANGE IN THE OXIDATION OF AN ALCOHOL TO AN ACID

Entropy of the liquid alcohol		Entropy of the crystalline acid		Entropy decrease during oxidation
CH_3OH	32.6	HCO_2H	25.3	7.3
C_2H_5OH	42.3	CH_3CO_2H	36.4	5.9
$C_2H_4(OH)_2$	42.9	$(CO_2H)_2$	30.4	6.2 × 2

In view of the foregoing considerations, we now feel justified in suggesting the hypothesis that the entropy of an organic compound is quite definitely related to its constitution. Indeed, aside from the evidence presented in this paper, such a relationship seems inherently plausible in the light of the well-established correlation between structure and such thermal data as the heats of combustion and heats of formation.[13] We,

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[11] As methyl alcohol, the first member of this series, melts far below room temperature, a corresponding extrapolation in its case would be very uncertain and hence hardly worth while.

[12] Linhart, *J. Gen. Physiol.*, **2**, 250 (1920).

[13] For a brief consideration of some of these correlations the reader is referred to Cohen, "Organic Chemistry for Advanced Students," Edward Arnold, London, 1921, Part 2, pp. 56–70.

therefore, believe that with the accumulation of further data it will become possible to predict the entropies of many organic compounds, just as we have estimated that of mannitol, with a fair degree of approximation.

The Free Energies of Organic Compounds

To the chemist, the free energy of formation of a compound is of greater interest than its entropy. Accordingly, we have also calculated the free energies of the eight substances by means of the third law of thermodynamics and the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

For obtaining the figures for the ΔH of formation of the various compounds we have tried to select the most reliable value for the heat of combustion of each substance after consulting the Landolt-Börnstein "Tabellen" and also in several cases the original literature.[14] The chosen data, expressed in 15° calories, appear in Col. 2 of Table V. The ΔH values were then calculated by use of 68,270 cal. and 94,250 cal. for the heats of combustion of hydrogen and graphite carbon,[15] respectively. Col. 4 contains the entropy of formation for each compound, which is simply the difference between its S_{298} and the corresponding values[16] for the various elements contained therein.

Table V

Thermal Data

The 15° calorie is used throughout

Substance	Heat of combustion at constant pressure Cal.	ΔH_{298} Cal.	ΔS_{298} Entropy units	ΔF_{298} Cal.
*iso*Propyl alcohol	478,300	− 77,500	−100.0	− 47,700
Acetone	430,400	− 57,200	− 64.2	− 38,000
Glycol	282,200	−111,100	− 96.0	− 82,500
Glycerol	397,200	−158,600	−140.5	−116,700
Acetic acid	209,600	−115,400	− 63.2	− 96,600
Palmitic acid	2,389,000	−211,000	−409.9	− 89,000
Oxalic acid	60,200	−196,600	− 97.6	−167,500
Glucose	674,000	−301,100	−275.0	−219,100

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[14] Landolt-Börnstein-Roth-Scheele "Tabellen," **1923**. For glycol, glucose and oxalic acid we have relied entirely on Stohmann's determinations. For acetone and glycerol we have used the values of Emery and Benedict. In the case of palmitic acid, the value selected represents a weighted mean between the result of Stohmann and that obtained by Emery and Benedict in which the latter is given double weight. For *iso*propyl alcohol Zubow and Thomson both found a heat of combustion about 5500 cal. below that of *n*-propyl alcohol, and accordingly in the present instance we have subtracted this amount from the very accurate value for the normal alcohol obtained by Richards and Davis. In the case of acetic acid there seems to be no way of reconciling the results of Berthelot and Thomson, which are, respectively, 209,600 cal. and 219,000 cal. per mole for the acid in the liquid state; in Table V we have tentatively employed the former value.

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

[16] Ref. 15, p. 464.

The resulting free energies appear in the last column and, with the exceptions of acetic and palmitic acids, are probably not in error by more than one or two thousand calories. In the case of palmitic acid the accuracy of the result is largely limited by that of the heat of combustion, which is very large and may easily be in error by five or six thousand calories. The uncertainty with regard to acetic acid has a somewhat similar origin. Berthelot's value for the heat of combustion gives us a free energy of —96,600 cal., while Thomson's value gives —87,000 cal. The discrepancy is remarkably large and it seems hard to say which result is more reliable.

Even with the foregoing elements of uncertainty, the data seem to indicate several regularities in the free energies of the organic compounds that have been studied. Thus, the free energy of formic acid, as determined with the aid of the specific-heat results of Gibson, Latimer and Parks,[10] is —86,400 cal., while Branch's equilibrium data[17] give —84,900 cal. Evidently, the true value cannot be far from —85,500 cal. For acetic acid we have the values given in the preceding paragraph and for palmitic acid the result is —89,000. Hence, if Berthelot's value for the heat of combustion of acetic acid be the correct one, there is a free energy decrease of about 11,000 cal. in going from the first member of the series to the second. On the other hand, in the jump from acetic acid to palmitic acid the change is certainly a relatively small one and well within the limit of error of the data involved. Apparently in the fatty acid series, with the possible anomaly of formic acid, the introduction of each CH_2 group into the chain involves no appreciable free-energy change. This is in entire accord with the conclusions of the previous study on primary alcohols.[1]

Another regularity is indicated by the data in Table VI.

TABLE VI

FREE-ENERGY CHANGE ACCOMPANYING THE INTRODUCTION OF AN HYDROXYL GROUP

Initial liquid and its free energy			Resulting liquid and its free energy		Difference in free energy
CH_4[a]	−9,800	⟶	CH_3OH	−44,500	−34,700
C_2H_5OH	−44,000	⟶	$C_2H_4(OH)_2$	−82,500	−38,500
iso C_3H_7OH	−47,700	⟶	$C_3H_5(OH)_3$	−116,700	−34,500 × 2

[a] Lewis and Randall (Ref. 15, p. 572) give —12,800 cal. as the free energy of gaseous methane. Hildebrand ("Solubility," Chemical Catalog Company, New York, **1924**, p. 34) finds by extrapolation of the vapor-pressure curve of the liquid at lower temperatures the value of 370 atm. for methane if it were to exist as a liquid at 298° K. On this basis we have estimated the fugacity of liquid methane at 1 atm. and 298° K. as 160 atm. and have arrived at the value, —9,800 cal., for the free energy.

Apparently, the substitution of an hydroxyl group for a hydrogen atom in a compound involves a fairly regular free-energy decrease of about 35,500 cal. when all the substances considered are in the liquid state. Using

[17] Branch, THIS JOURNAL, **37**, 2316 (1915).

this result and bearing in mind that each CH_2 group introduced into a chain causes no appreciable free-energy change, we might predict that liquid mannitol has a free energy 106,500 cal. lower than that of glycerol, or about —223,200 cal. Of course, mannitol exists in the crystalline rather than in the liquid state at 298° K. but the decrease in going from the liquid to the solid state is probably only a few thousand calories, as the data of Gibson and Giauque indicate that at a temperature 100° below the melting point $\Delta F = -1150$ cal. per mole for the process: glycerol (liquid) $\longrightarrow$ glycerol (crystalline). In view of these considerations, it is interesting to note that Linhart's calculations, revised by means of the newer atomic entropies, give —225,300 cal. for the ΔF_{298} of formation of crystalline mannitol, while our predicted entropy of 58.7 units gives —225,900 cal.

Still another interesting point concerns the comparative free energies of a primary and a secondary alcohol. While as yet we have been unable to determine the free energy of *n*-propyl alcohol, the regularity observed in the neighboring members of its series enables us to predict the value —44,200 cal. with a good deal of confidence. The result obtained for *iso*-propyl alcohol is about 3,500 cal. lower than this. From the thermodynamic standpoint the *iso* compound is thus the more stable of the two.

Summary

1. The specific heats of *iso*propyl alcohol, acetone, ethylene glycol, acetic acid and palmitic acid have been measured over a range of temperatures. The heats of fusion of the first four substances have also been determined.

2. The entropies of eight organic compounds have been calculated and certain regularities in the entropy values have been discovered.

3. The corresponding free energies have also been calculated. Apparently there is no free-energy change for a CH_2 increment in an homologous series. On the other hand, a decrease of 35,500 cal. accompanies the substitution of an hydroxyl group for a hydrogen atom in an organic compound.

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