for cells C, the equation $E_t = 0.00037 + 0.462\ E - 0.211\ E^2$ was obtained by the method of averages.[5] From this were obtained the values of $N_{\mathrm{Ba}} = \mathrm{d}E_t/dE = 0.462 - 0.422\ E$ given in Col. 6 of Table II. The transference numbers determined from Cell B agree with those determined from cell C within 0.2%.

Summary

1. The electromotive forces of concentration cells of barium bromide, both with and without transference, have been measured. From these data the transference numbers have been calculated.
2. The geometric mean activity coefficients have been calculated and are found to agree closely with those calculated for barium chloride from freezing-point data.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. III. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF TERTIARY BUTYL ALCOHOL, MANNITOL, ERYTHRITOL AND NORMAL BUTYRIC ACID

BY GEORGE S. PARKS AND C. TRAVIS ANDERSON

RECEIVED FEBRUARY 13, 1926 PUBLISHED JUNE 5, 1926

In the preceding paper[1] of this series the hypothesis was suggested that the entropy of an organic compound is related in a simple definite manner to its constitution. At that time considerable data were adduced in support of this hypothesis which, moreover, seems inherently plausible in view of the well-known regularities in other thermal properties, such as the heats of formation, of organic substances. However, we have believed that the proposition should be further tested. With this end in mind, we have now determined the heat capacities of four compounds, namely, *tert.*-butyl alcohol, mannitol, erythritol and *n*-butyric acid, in order that the entropies obtainable thereby might be compared with the values predicted from the constitution.

Materials

tert.-Butyl Alcohol.—A good grade of *tert.*-butyl alcohol (m. p., 20°) was first dehydrated by distillation over lime in the ordinary manner. The resulting distillate was then subjected to eight successive fractional crystallizations. The final product melted at 25.4° as measured in the heat of fusion determinations. De Forcrand[2] has

---

[5] Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, **1918**, p. 163.

[1] Parks and Kelley, THIS JOURNAL, **47**, 2094 (1925).

[2] de Forcrand, *Compt. rend.*, **136**, 1034 (1903).

reported a melting point of 25.53°, while Norris and Ashdown[3] recently obtained 24.3° for a sample of this alcohol.

Mannitol and Erythritol.—The mannitol and erythritol were Eastman products, which were used without further purification. Their freezing points, determined with a thermometer which had been calibrated by the United States Bureau of Standards, were 166.0° and 118.9°, respectively, during practically the entire solidification process. These compounds were apparently free from inorganic impurities, since samples on ignition left no residue.

Butyric Acid.—In the case of butyric acid difficulty was experienced in purchasing a sample satisfactory for further purification. The material finally employed was Kahlbaum's "special, synthetic" *n*-butyric acid (m. p., about —10°). It had an average boiling point of 162.7°, with a distillation range of about 1°. This material was subjected to twelve successive fractional cystallizations.

Unfortunately, the final product was not as pure as we had at first believed. The chief impurity was undoubtedly water, although in the sample studied there was also present a small amount of copper butyrate, produced by corrosion of the calorimeter. The melting point, observed in connection with the heat of fusion determinations, was —5.7°. This temperature, on the basis of Faucon's investigation[4] and on the assumption that water was the sole impurity, corresponds to a sample containing 99.1% of *n*-butyric acid.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in a previous paper.[5] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except perhaps for butyric acid in which case impurities in the sample used may also influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie and with all weights reduced to a vacuum basis, appear in Tables I and II, respectively. On the whole these experimental values compare fairly well with the meager data in the literature.[6] The two results of de Forcrand for *tert.*-butyl alcohol are within 1% of ours, as is also the case with Kopp's value for mannitol. Magie's determination on mannitol is, however, 2% above our curve; while Luginine's results at 60° for mannitol and erythritol fall 5% and 2%, respectively, below our extrapolated curves. The heat of fusion of *tert.*-butyl alcohol obtained by de Forcrand is 4% below our value; that of Guillot for butyric acid, 5%. Possibly our relatively higher fusion values arise from our assumption that the marked increase in specific heat as the melting point is approached is due to premelting and should be included in the heat of fusion. Whether justifiable,

---

[3] Norris and Ashdown, This Journal, **47**, 842 (1925).

[4] Faucon, *Ann. chim. phys.*, [8] **19**, 97 (1910).

[5] Parks, This Journal, **47**, 338 (1925).

[6] Landolt-Börnstein-Roth-Scheele, "Tabellen," Julius Springer, Berlin, **1923**, pp. 1265, 1471.

or not, this view causes no appreciable error in the ensuing entropy calculations.

TABLE I

SPECIFIC HEATS

tert.-BUTYL ALCOHOL

CRYSTALS

Temp., °K.	87.1	93.2	99.8	102.5	106.1	108.2	112.3	153.5	160.7
C_p per g.	0.178	0.188	0.198	0.200	0.207	0.210	0.216	0.282	0.290
Temp., °K.	193.0	196.7	199.7	203.5	216.0	228.3	243.4	275.0	275.0
C_p per g.	0.342	0.349	0.354	0.362	0.385	0.408	0.443	0.560	0.563

LIQUID

Temp., °K.	300.0	300.3
C_p per g.	0.725	0.728

MANNITOL

CRYSTALS ONLY

Temp., °K.	88.5	94.4	95.9	101.5	102.0	107.3	108.2	111.1	118.3
C_p per g.	0.107	0.113	0.115	0.121	0.121	0.127	0.128	0.131	0.137
Temp., °K.	153.0	160.3	193.2	198.0	201.6	275.0	275.0	291.0	294.1
C_p per g.	0.171	0.178	0.209	0.214	0.218	0.290	0.289	0.307	0.310

ERYTHRITOL[a]

CRYSTALS ONLY

Temp., °K.	87.0	92.3	94.7	99.0	99.6	101.2	105.6	106.0
C_p per g.	0.110	0.116	0.119	0.124	0.124	0.127	0.131	0.131
Temp., °K.	111.7	186.0	193.5	200.5	275.3	275.5	289.0	291.7
C_p per g.	0.137	0.212	0.219	0.227	0.300	0.300	0.315	0.317

n-BUTYRIC ACID

CRYSTALS

Temp., °K.	89.2	94.8	100.9	107.9	112.9	152.4	161.4	186.0	193.4
C_p per g.	0.172	0.179	0.187	0.195	0.201	0.253	0.266	0.314	0.335
Temp., °K.	197.5	200.0	204.4	211.3	215.2	215.9	221.0	226.2	231.5
C_p per g.	0.349	0.358	0.374	0.405	0.430	0.436	0.470	0.355	0.368

LIQUID

Temp., °K.	274.8	275.1	276.1	288.1	290.7
C_p per g.	0.464	0.464	0.464	0.475	0.478

[a] In this connection we wish to acknowledge our indebtedness to Mr. Hugh M. Huffman of this Laboratory, who very kindly made about half of the measurements on erythritol for us.

TABLE II

FUSION DATA

Substance	M. p. °K.	Heat of fusion (Cal. per g.) 1st result	2nd result	Mean
tert.-Butyl alcohol	298.5	21.88	21.89	21.88
n-Butyric acid	267.4	29.97	30.10	30.04

Practically all organic compounds melting above 250°K., thus far investigated show an essentially similar curve when specific heats are plotted against temperatures. From about 100° to somewhat above 200°K. this characteristic curve is nearly straight. In the present instance *tert.*-butyl alcohol, mannitol and erythritol show the linear relationship but the butyric acid crystals present an interesting exception. Their specific-heat curve begins to rise abnormally above 150° and finally attains a maximum at about 221°K., above which point there is a sharp 25% decrease within a couple of degrees. The measurements were strictly reproducible and seem to indicate a transition in the crystalline acid, which is rather gradual as regards temperature. The whole phenomenon appears similar to that which Simon[7] found in the case of ammonium chloride. Possibly, it may be related in some way to the impurities in our material, although this hypothesis we regard as extremely doubtful, especially as the time-temperature curve in the fusion process was normal and reasonably sharp.

Discussion

Entropies of the Compounds.—Using the data contained in Tables I and II, we have calculated the entropies at 298.1°K. for crystalline mannitol and erythritol and for liquid *tert.*-butyl alcohol and *n*-butyric acid. In these calculations, as previously, we have employed the "*n* formula" of Lewis and Gibson[8] for estimating the entropy increases for the crystals, Col. 2 of Table III, from zero absolute to 90°K. The various entropy increments from 90° to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from our experimental data. The results for the total entropy in calories per degree appear under the heading S_{298} in the last column.

TABLE III

ENTROPIES OF THE SUBSTANCES PER MOLE

Substance	Crystals		Fusion	Liquid	S_{298}
	0–90°K.	Above 90°K.			
tert.-Butyl alcohol	12.75	29.04	5.43	..	47.2
Mannitol	18.80	41.68	..	..	60.5
Erythritol	13.26	29.25	..	..	42.5
n-Butyric acid	19.70	27.09	9.78	4.43	61.0

These experimental values for S_{298} may now be compared with those which might be predicted from a consideration of the constitution of the

---

[7] Simon, *Ann. Physik*, **68**, 264 (1922).

[8] Lewis and Gibson, THIS JOURNAL, **39**, 2565 (1917). In our opinion the "*n* formula," when applied to organic compounds, constitutes only a rough first approximation. The estimates thereby obtained for the entropies below 90°K. may quite possibly be in error, in an absolute sense, to the extent of 10 or 20%. However, as a means of extrapolation below the temperatures for which we have experimental data, the formula is easy to apply and is probably as satisfactory for organic compounds as any that have been suggested. Furthermore, in all probability its application to several similar substances involves comparable errors and, hence, we feel confident that its use in this series of papers will not invalidate the comparisons drawn.

Of course, if specific-heat data down to extremely low temperatures (to 10°K., for instance) should become available for a number of representative organic compounds, a more satisfactory and accurate extrapolation formula might be developed. However, we believe that in this event all our S_{298} values will be changed by approximately the same percentage and that the revised values, though more accurate in an absolute sense, will stand in essentially the same relative positions as at present.

four compounds in question. Thus in the preceding papers of this series the entropies of ethyl, *n*-butyl and *iso*propyl alcohols were found to be 42.3, 60.2 and 45.6 units, respectively. By interpolation S_{298} for *n*-propyl alcohol should be 51.3 and thus it appears that *iso*propyl alcohol has an entropy 5.7 units below the corresponding primary alcohol. By analogy a tertiary alcohol might be expected to have an entropy value 2×5.7 or 11.4 units below the corresponding primary compound. This reasoning would then lead us to predict a value of $60.2 - 11.4$ or 48.8 for S_{298} in the case of *tert.*-butyl alcohol. The result actually obtained from the heat-capacity data is 1.6 cal. per degree below this value.

In the second article of this series the S_{298} values for crystalline glycol and crystalline glycerol were estimated to be 30.7 and 37.7, respectively, and on the basis of this increase of 7.0 units per CH(OH) increment the entropy of mannitol at 298°K. was predicted to be $37.7 + 3(7.0)$ or 58.7 cal. per degree. The experimental result just found is 1.8 units above this predicted value. By the same reasoning we might predict for crystalline erythritol $37.7 + 7.0$ or 44.7 cal. per degree, while 42.5 is the figure obtained for the specific-heat measurements.

Furthermore, in the preceding paper the entropy of acetic acid was found to be 46.3 and the average increase per CH_2 increment in going from acetic acid to liquid palmitic acid at 298°K. was calculated to be 8.6 entropy units. Hence, the predicted value for *n*-butyric acid is $46.3 + 2(8.6)$ or 63.5; the experimental result is 2.5 units below this prediction.

Thus we have four comparisons between the entropies obtained experimentally and those calculated on the hypothesis that the entropy of an organic compound in any given series is definitely related in an additive manner to its constitution. In these four cases the average difference is 2.0 units or 3.9%, and in view of this fact we now feel justified in concluding that the foregoing hypothesis is approximately valid.

The Free Energies of the Four Compounds

We have also calculated the free energies of these four compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$. For obtaining the values 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.[9] The chosen data, expressed in 15° calories, appear in Col. 2 of Table IV. The ΔH values were then calculated by use of 68,270 cal. and 94,250 cal. for

[9] Landolt-Börnstein-Roth-Scheele, "Tabellen." For *tert.*-butyl alcohol we have used the Zubow-Swietoslawski value at 18° but have recalculated it for 25° in order that it might thus be on a strictly comparable basis with the data for the alcohols previously studied. For mannitol and erythritol we have employed in each case a mean of the two results of Stohmann and that of Berthelot, thus giving the former's work double weight. In the case of *n*-butyric acid we have relied entirely on Stohmann's determination.

the heats of combustion of hydrogen and graphitic carbon,[10] respectively. Col. 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values[11] for the various elements contained therein. The resulting free energies appear in the last column and are probably not in error by more than one or two thousand calories.

TABLE IV

THERMAL DATA

Substance	Heat of combustion at constant pressure Cal.	ΔH_{298} Cal.	ΔS_{298} Entropy units	ΔF_{298} Cal.
tert.-Butyl alcohol	630,000	− 88,400	−129.2	− 49,900
Mannitol	728,500	−314,900	−297.4	−226,200
Erythritol	504,100	−214,800	−205.9	−152,900
n-Butyric acid	524,800	−125,300	−110.0	− 92,500

Obviously, if the ΔH and ΔS of formation of an organic compound change in a regular manner with its constitution, the free energy of formation, ΔF, also must undergo a regular variation. Employing the reasoning of the preceding section and utilizing data from the earlier papers, we therefore predict the value, —51,100 cal., for *tert.*-butyl alcohol. The difference between this prediction and the experimental result appearing in Table IV is only 1200 cal., an amount which is less than the possible error in the heat of combustion of this compound.

Likewise we might predict for liquid mannitol and liquid erythritol the free energy values, —223,200 cal. and —152.200 cal., respectively. Of course, these two compounds exist normally in the crystalline state at 298°K., but the free-energy decrease in going from the liquid to the solid state must be comparatively small. On the basis of the data of Gibson and Giauque[12] which indicate that at a temperature 100° below the melting point ΔF = —1150 cal. per mole for the process, glycerol (liquid) ⟶ glycerol (crystalline), we have estimated these respective decreases in the cases of mannitol and erythritol to be 3200 cal. and 1400 cal. Hence our predicted values are approximately —226,400 cal. and —153,600 cal. for these compounds in the crystalline state. Their agreement with the experimental results is remarkably good.

Finally, by interpolation between the free energies of acetic and palmitic acids, the predicted value for butyric acid is found to be —91,600 (±5000) cal., a value which compares favorably with that obtained experimentally. However, in view of the large possible error in this predicted value, too much weight must not be given to this particular comparison.

---

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

[11] Ref. 11, p. 464.

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

Summary

1. The specific heats of *tert.*-butyl alcohol, mannitol, erythritol and *n*-butyric acid have been measured over a wide range of temperatures. The heats of fusion of *tert.*-butyl alcohol and *n*-butyric acid have also been determined.

2. The entropies and free energies of the four compounds have been calculated by means of these heat-capacity data. The experimental results thus obtained are in good agreement with the entropy and free-energy values predicted for these substances upon the basis of previously observed regularities.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND CHEMISTRY OF OHIO STATE UNIVERSITY]

INFRA-RED ABSORPTION IN ETHERS, ESTERS AND RELATED SUBSTANCES

BY ALPHEUS W. SMITH AND CECIL E. BOORD

RECEIVED FEBRUARY 15, 1926 PUBLISHED JUNE 5, 1926

By a study of the absorption spectra of a number of hydrogen-carbon compounds in the region between 0.9 μ and 2.4 μ Ellis[1] has been able to show that in such compounds there appears to be a harmonic relationship between the absorption bands. He attributes this series of bands to the hydrogen-carbon linkage in the molecule. Except for the observations of Dreisch[2] on benzene and chloroform and those of Coblentz[3] on lard oil, there are few detailed data on the absorption of hydrogen-carbon compounds in this region of the spectrum. The more comprehensive work of Coblentz[4] and that of Weniger[5] covered the spectral region as far as about 15 μ but they did not study the near infra-red with sufficient detail to locate many of the bands which Ellis arranges in a harmonic series. It seemed of interest, therefore, to make some observations on other hydrogen-carbon compounds to see in how far this series of bands remains unchanged with the introduction of various groups into the molecular structure.

Apparatus

Spectrometer.—The spectrometer (Fig. 1), which was a standard Hilger instrument for the infra-red region of the spectrum, was provided

---

[1] Ellis, *Phys. Rev.*, [2] **23**, 48 (1924); *J. Optical Soc. Am.*, **8**, 1 (1924).

[2] Dreisch, *Z. Physik*, **30**, 200 (1924).

[3] Coblentz, *Bur. Standards, Sci. Papers*, No. 148, **1921**.

[4] Coblentz, "Infra-red Absorption Spectra," Part I, *Carnegie Inst. Pub.*, No. **35**, (1905).

[5] Weniger, *Phys. Rev.*, **31**, 388 (1910).