

*Anal.* Subs., 0.2354: CO<sub>2</sub>, 0.3629; H<sub>2</sub>O, 0.1031. Subs., 0.1517: AgI, 0.048. Calcd. for C<sub>20</sub>H<sub>30</sub>O<sub>17</sub>I: C, 41.82; H, 4.73; I, 17.01. Found: C, 42.04; H, 4.94; I, 17.10.

### Summary

The specific-rotational values reported in the literature for chloro-, bromo- and iodo-hepta-acetyl cellobiose have been revised. In addition to the fluoro-hexa-acetyl and octo-acetyl compounds, the fluoro, chloro-, bromo- and iodo-hepta-acetyl derivatives of 4-glucosido-mannose have been prepared and described. A comparison of the specific rotational values shows that these two sets of *biose* derivatives deviate from the regular relationship observed for the corresponding derivatives of the *monose* sugars. An agreement is, however, obtained by excluding the values for the fluoro derivatives. When studied for other bioses these deviations may lead to a more detailed knowledge of the spatial arrangement of the atoms in the bioses.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]  
**THERMAL DATA ON ORGANIC COMPOUNDS. IV. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF NORMAL PROPYL ALCOHOL, ETHYL ETHER AND DULCITOL**

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RECEIVED JUNE 25, 1926

PUBLISHED NOVEMBER 5, 1926

In three earlier papers<sup>1</sup> it has been shown that the entropy and free energy of an organic compound are related to its constitution in a simple additive manner. In the present investigation, heat-capacity data for *n*-propyl alcohol, ethyl ether and dulcitol have been obtained and thereby the corresponding entropies and free energies have been calculated. These new results enable us to test further the above proposition. Moreover, the results accumulated thus far permit an interesting comparison to be made between the entropies and free energies of three sets of isomers, namely, *n*- and *isopropyl* alcohol, ether, *n*-butyl alcohol and *tert.*-butyl

TABLE I

THE ENTROPIES AND FREE ENERGIES OF SOME ISOMERS AT 298°K.

Substance	M. p., °K.	Entropy	Free energy, cal.	
C <sub>3</sub> H <sub>8</sub> O	<i>n</i> -Propyl alcohol	147.0	51.2	-44,100
	<i>iso</i> Propyl alcohol	184.6	45.6	-47,700
C <sub>4</sub> H <sub>10</sub> O	Ethyl ether	156.8	67.7	-33,600
	<i>n</i> -Butyl alcohol	183.9	60.2	-44,100
	<i>tert.</i> -Butyl alcohol	298.5	47.2	-49,900
C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	Mannitol	439.1	60.5	-226,200
	Dulcitol	461	59.2	-228,100

<sup>1</sup> Parks, *THIS JOURNAL*, 47, 338 (1925). Parks and Kelley, *ibid.*, 47, 2094 (1925). Parks and Anderson, *ibid.*, 48, 1506 (1926).

alcohol, and the two stereo-isomers, mannitol and dulcitol. The data for this comparison are summarized in Table I which seems to indicate that in the case of isomers the compound with the lowest melting point has the largest entropy and free energy.

### Materials

***n*-Propyl Alcohol.**—Two samples of *n*-propyl alcohol were used in the present investigation. Sample A was prepared from Eastman's "refined" propyl alcohol by treatment and distillation with lime in the ordinary manner. The resulting product was carefully fractionated and the middle third was selected for use in the measurements. It had a boiling range of 0.05° and a density of 0.8010 at 25°/4°. Sample B was very kindly given to us by the late Professor Roger F. Brunel of Bryn Mawr College. It had been very carefully purified by him and probably represents the purest *n*-propyl alcohol ever obtained.<sup>2</sup> Brunel's determination of its density at 25°/4° gave 0.7998; our own determination, made just before the measurements, gave 0.7999.

These two samples yielded identical results in the specific determinations on the liquid, but Sample A apparently contained impurities which prevented complete crystallization. Sample B, on the other hand, could be crystallized completely and was then found to have a very sharp melting point. Consequently, it was employed in the determinations on the crystals and in measuring the heat of fusion. The measurements on the glass were made upon Sample A, subsequent to rapid cooling with liquid air.

**Ethyl Ether.**—Pure, absolute ethyl ether was twice treated with metallic sodium and allowed to stand for periods of several months. It was finally fractionated carefully, the middle third being employed in the present measurements. Its melting point was sharp, indicating a high degree of purity.

**Dulcitol.**—The dulcitol was a c.p. Pfanstiehl product, melting at 188° and containing 0.1% of water. It was free from non-volatile inorganic impurities, as a sample on ignition left no residue.

### 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 the first paper of this series. 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 the *n*-propyl alcohol glass. In this particular case 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 incipient crystallization which made measurements in the temperature range 115–147°K. impossible.

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 II and III, respectively. For comparison with these values the literature to date contains only very meager data.<sup>3</sup> Bose's determination of the

<sup>2</sup> Brunel, *THIS JOURNAL*, **45**, 1335 (1923).

<sup>3</sup> Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1265.

specific heat of *n*-propyl alcohol at 275°K. is within 0.2% of ours and in general our results for this substance in the liquid and glassy state are in fair agreement with the earlier work of Gibson, Parks and Latimer,<sup>4</sup> the percentage differences at the three temperatures 275°, 200° and 90°K., being 1.5, 0.0 and 4.0%, respectively. In the case of ether, the values

TABLE II  
SPECIFIC HEATS  
*n*-PROPYL ALCOHOL

Glass and liquid (Sample A)								
Temp., °K. ....	86.4	91.5	96.0	100.0	103.7	108.0	112.6	169.1
$C_p$ per g. ....	0.233	0.255	0.333	0.432	0.426	0.425	0.424	0.430
Temp., °K. ....	185.9	193.5	197.7	201.6	275.1	275.3	275.3	
$C_p$ per g. ....	0.438	0.441	0.444	0.447	0.531	0.531	0.531	
Crystals (Sample B)								
Temp., °K. ....	88.3	94.2	100.2	101.1	107.0	113.3	113.6	
$C_p$ per g. ....	0.207	0.216	0.226	0.227	0.237	0.246	0.246	
Temp., °K. ....	122.1	122.8	127.7					
$C_p$ per g. ....	0.281	0.262	0.272					
Liquid (Sample B)								
Temp., °K. ....	152.1	152.6	185.6	194.1	199.0	275.0	275.0	
$C_p$ per g. ....	0.425	0.425	0.436	0.442	0.444	0.531	0.531	
ETHYL ETHER <sup>a</sup>								
Crystals								
Temp., °K. ....	76.1	82.5	89.1	93.4	95.5	96.7	98.3	
$C_p$ per g. ....	0.201	0.212	0.222	0.227	0.233	0.233	0.236	
Temp., °K. ....	103.4	103.7						
$C_p$ per g. ....	0.244	0.244						
Temp., °K. ....	110.5	110.8	112.0	114.5	123.3	123.4	131.1	135.2
$C_p$ per g. ....	0.254	0.255	0.256	0.259	0.271	0.271	0.283	0.287
Liquid								
Temp., °K. ....	164.4	186.1	195.6	201.6	205.5	213.5	275.2	
$C_p$ per g. ....	0.475	0.490	0.498	0.501	0.505	0.507	0.544	
Temp., °K. ....	280.2	286.0	290.0					
$C_p$ per g. ....	0.547	0.549	0.551					
DULCROL								
Crystals only								
Temp., °K. ....	88.5	96.0	101.7	105.7	107.5	110.3	121.8	
$C_p$ per g. ....	0.103	0.112	0.118	0.123	0.125	0.127	0.139	
Temp., °K. ....	127.3	151.7	161.0					
$C_p$ per g. ....	0.145	0.169	0.178					
Temp., °K. ....	186.0	193.9	198.0	202.8	275.6	276.0	287.0	
$C_p$ per g. ....	0.203	0.210	0.215	0.219	0.294	0.295	0.307	
Temp., °K. ....	290.1	292.8						
$C_p$ per g. ....	0.310	0.313						

<sup>a</sup> In all cases ethyl ether, on being cooled, first crystallized in an unstable modification with a melting point at 149.7°K. On further cooling, a transformation into the stable form (m. p., 156.8°K.) took place. It is to the latter form that all the data in the present paper apply.

<sup>4</sup> Gibson, Parks and Latimer, *THIS JOURNAL*, **42**, 1545 (1920).

TABLE III  
 FUSION DATA

Substance	M. p., °K.	Heat of fusion (Cal. per g.)		
		1st result	2nd result	Mean
<i>n</i> -Propyl alcohol. . . . .	147.0	20.62	20.69	20.66
Ethyl ether. . . . .	156.8	23.49	23.59	23.54

for our curve at 275°K. are about 2% above the respective values obtained by Regnault and Nadejdin, although they are more than 4% below the recent determinations of Keyes and Beattie.<sup>5</sup> At 200°K. our values are about 3% below those obtained by Batelli for liquid ether. For dulcitol the only value in the literature, that of Magie at 293°K., is about 10% below our curve.

### Discussion

**Entropies of the Compounds.**—Using the data contained in Tables II and III, we have calculated the entropy at 298.1°K. for liquid *n*-propyl alcohol and ethyl ether and for crystalline dulcitol. In these calculations, as previously, we have employed the “*n* formula” of Lewis and Gibson<sup>6</sup> for estimating the entropy increases for the crystals, Col. 2 of Table IV, from 0° 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 IV  
 ENTROPIES OF THE SUBSTANCES PER MOLE

Substance	Crystals		Fusion	Liquids	$S_{298}$
	0–90°K.	Above 90°K.			
<i>n</i> -Propyl alcohol. . . . .	15.50	7.42	8.44	19.83	51.2
Ethyl ether. . . . .	21.20	10.98	11.12	24.35	67.7
Dulcitol. . . . .	17.53	41.64	...	...	59.2

In the preceding paper, from a consideration of the constitution of the compounds, the values 51.3 and 58.7 were predicted for  $S_{298}$  in the cases, respectively, of *n*-propyl alcohol and of a substance like mannitol or dulcitol. The experimental values just obtained are in remarkable agreement with these two predictions.

The heat-capacity data for the *n*-propyl alcohol glass permit us to make a rough estimate of its entropy at the absolute zero. The excess of entropy of the glass over the crystals at 86°K.,  $\Delta S_{86}$ , is given by the equation

$$\Delta S_{86} = \frac{\Delta H (\text{fusion})}{147.0} - \int_{86.0}^{147.0} \frac{C_{p, \text{glass}} - C_{p, \text{crystals}}}{T} dT$$

<sup>5</sup> Keyes and Beattie, *THIS JOURNAL*, **46**, 1759 (1924).

<sup>6</sup> Lewis and Gibson, *ibid.*, **39**, 2565 (1917). In the case of *n*-propyl alcohol we have data for the crystals over only a short range of temperatures and consequently any value for “*n*” thus obtained would be extremely uncertain. As the values calculated previously for ethyl and *n*-butyl alcohol are 0.305 and 0.298, we have therefore taken the mean of these (0.301) for *n*-propyl alcohol in the present instance.

and amounts to 3.61 units per mole. At 86°K. the entropy of the crystals, calculated with the aid of the Lewis-Gibson "*n* formula," is 14.94 and the specific heat of the glass is 11.5% greater than that of the crystalline form. If this same percentage excess in heat capacity should continue to the lowest temperatures, the decrease in entropy of the glass from 86° to 0°K. would be greater than the corresponding decrease for the crystals by 1.72 units per mole. In this event the entropy of the glass at the absolute zero would exceed that of the crystals by 1.89 units per mole. This result is similar to that obtained by one of us in the case of ethyl alcohol glass<sup>7</sup> and to that obtained by Gibson and Giauque<sup>8</sup> in the case of glycerol glass.

### The Free Energies of the Three Compounds

We have also calculated the free energies of these three compounds 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  $\Delta H$  of formation we have tried to select the most reliable value for the heat of combustion of each substance. For *n*-propyl alcohol we have utilized the result obtained by Richards and Davis<sup>9</sup> at 18°, recalculated in terms of the 15° calorie for the standard temperature of 25°. For ethyl ether we have relied entirely upon Stohmann's determination. In the case of dulcitol we have employed a weighted mean between the results of Stohmann and Berthelot, in which the work of the former was given double weight. The chosen data appear in Col. 2 of Table V. Cols. 3 and 4 contain the values for the  $\Delta H$  of formation and the entropy of formation, calculated by the usual methods. The resulting free energies are given in the last column.

TABLE V  
THERMAL DATA

Substance	Heat of combustion at constant pressure, Cal.	$\Delta H_{298}$ , Cal.	$\Delta S_{298}$ , Entropy units	$\Delta F^{\circ}_{298}$ , Cal.
<i>n</i> -Propyl alcohol.....	483,520	-72,260	-94.5	-44,100
Ethyl ether.....	652,300	-66,000	-108.7	-33,600
Dulcitol.....	726,200	-317,200	-298.7	-228,100

In the case of *n*-propyl alcohol, Parks and Kelley have predicted the free-energy value, -44,200 cal. The experimental result, -44,100 cal., is in excellent agreement with this prediction. For crystalline mannitol Parks and Anderson predicted the value -226,400 cal., and by similar reasoning we might now suggest for crystalline dulcitol -226,900 cal.

<sup>7</sup> Parks, Ref. 1.

<sup>8</sup> Gibson and Giauque, *THIS JOURNAL*, **45**, 94 (1923).

<sup>9</sup> Richards and Davis, *ibid.*, **42**, 1614 (1920). This result as it appears in their article is apparently involved in a typographical error. It should be 482,580, instead of 485,800 cal.

Here, again, the experimental result just obtained agrees well with the prediction.

In the case of ethyl ether it is interesting to note that our result of  $-33,600$  cal. checks fairly well with the value calculated from the equilibria data of Pease and Yung.<sup>10</sup> These investigators studied the equilibrium between ethyl alcohol, ether and water at the two temperatures,  $130^{\circ}$  and  $275^{\circ}$ . When used in conjunction with the value,  $-44,000$  cal., for the free energy of ethyl alcohol, their data give  $-33,900$  cal. for the free energy of ethyl ether. Recently the reliability of these equilibria measurements has been questioned by Clark, Graham and Winter,<sup>11</sup> who obtained conflicting data in a study of the same reaction at  $250^{\circ}$ ; but in the present instance our own free-energy value, obtained by an entirely different method, is certainly consistent with the result calculated from the work of Pease and Yung.

### Summary

1. The specific heats of crystalline and liquid *n*-propyl alcohol and ethyl ether and of crystalline dulcitol have been measured over a wide range of temperatures. The heats of fusion of the first two substances have also been determined and some data on the heat capacity of the super-cooled or glassy form of *n*-propyl alcohol have been obtained.

2. The entropies and free energies of the three compounds have been calculated from these heat-capacity data. The experimental results thus obtained are in good agreement with previous predictions.

3. The entropy of glassy *n*-propyl alcohol has been found to exceed that of the crystalline form by 3.61 units per mole at  $86^{\circ}\text{K}$ . and it seems improbable that this difference becomes zero at  $0^{\circ}\text{K}$ .

4. The accumulated data indicate that in the case of isomers the compound with the lowest melting point has the largest entropy and free energy.

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<sup>10</sup> Pease and Yung, *THIS JOURNAL*, **46**, 2404 (1924).

<sup>11</sup> Clark, Graham and Winter, *ibid.*, **47**, 2753 (1925).