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The Entropies of *n*-Butane and Isobutane, with Some Heat Capacity Data for Isobutane

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The entropies of *n*-butane ($S_{298}^{\circ}=75.8$ e.u.) and isobutane ($S_{298}^{\circ}=70.0$ e.u.) have been calculated from thermal data by the third law of thermodynamics. In this connection, heat capacity data for isobutane over the temperature range 79°–261°K have been obtained by the Nernst method and also, as a partial basis for these calculations, the mode of extrapolating entropies below liquid air temperatures has been critically examined. The discrepancies between these new results and the corresponding entropies obtained by statistical methods appear too large to be accounted for by errors in the thermal data or extrapolations involved. The thermodynamics of the isomerization reaction is briefly considered.

THE entropies of *n*-butane and isobutane, as well as of a number of other hydrocarbons, have recently been calculated by Kassel¹ by statistical methods. Omitting the contribution due to nuclear spin, he obtained 78.16 e.u. for *n*-butane and 74.04 e.u. for the *iso* compound at 298.1°K. Huffman, Parks, and Barmore² had previously measured the heat capacities of *n*-butane from 67° up to the boiling point and had calculated by the third law of thermodynamics an entropy value of 74.5 e.u. (erroneously reported as 74.4 e.u.). This discrepancy of nearly 3.7 e.u. between his value and the third law result Kassel then attributed to either an error in the extrapolation from 90°K to 0° by Parks, Huffman and Barmore or to "a zero-point entropy of the crystals caused by lack of equilibrium at the lower temperatures."

In this investigation we have critically re-examined the entropy calculations of Huffman, Parks and Barmore for *n*-butane and have thereby obtained $S_{298}^{\circ}=75.8$ e.u. as a more probable third law result. At the same time we have measured the heat capacities of isobutane from 79°K up to its boiling point and have likewise employed these data in calculating a value of $S_{298}^{\circ}=70.0$ e.u. Thus the discrepancies between the third law entropies and the results of Kassel's statistical calculations continue to be pronounced.

THE HEAT CAPACITY DATA FOR ISOBUTANE

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the heat of fusion of isobutane. The apparatus and details of experimental procedure have been fully described in other places.³ In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 0.7 percent; the fortuitous errors were usually under 0.25 percent. The results have been expressed in terms of the *defined* calorie (=4.185 absolute joules) per gram molecule, with all weights reduced to a vacuum basis.

The isobutane sample was specially prepared for us in the laboratory of the Shell Development Company by hydrogenation of very pure isobutane and by a subsequent series of careful fractional distillations of the resulting paraffin. From the change in melting point during the fusion determinations we estimated its purity to be about 99.7 mole percent. Incidentally, the melting point of pure isobutane was found to be 113.2°K, or almost 15° below the figure given in the *International Critical Tables*.⁴

Our various specific heat values (C_p) for the crystalline and liquid isobutane are given in Table I and are also represented graphically in Fig. 1. In addition, two independent determina-

¹ L. S. Kassel, J. Chem. Phys. **4**, 276 (1936).

² H. M. Huffman, G. S. Parks, and Mark Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).

³ G. S. Parks, J. Am. Chem. Soc. **47**, 338 (1925); also G. S. Parks and K. K. Kelley, J. Phys. Chem. **30**, 47 (1926).

⁴ *International Critical Tables* (1926), Vol. I, p. 188.

tions of the heat of fusion were made and these are given in Table II.

CALCULATION OF THE ENTROPIES

As the specific heat determinations on *n*-butane by Huffman, Parks and Barmore did not go below 67°K and those on isobutane in the present study extended to only 79°K, a fairly reliable method of extrapolating the entropies to the absolute zero is essential. In the present case we have employed the method of Kelley, Parks and Huffman.⁵

The extrapolation method

Kelley, Parks and Huffman in 1929 made a comparative study of the heat capacity curves for twelve organic compounds for which experimental data were available between 15° and 120°K. Seven of these compounds were aliphatic; incidentally these all contained oxygen and were more or less polar in character. The remaining five compounds possessed carbocyclic molecules and were either nonpolar or only moderately polar. While all twelve substances exhibited essentially similar heat capacity-temperature curves, those for the seven aliphatic compounds tended to fall off somewhat more rapidly with decreasing temperatures than those for the cyclic compounds. Subsequently these two groups were designated as "class I" and "class II," respectively. It was then an easy matter to develop an

TABLE I. Specific heats of isobutane in cal. per degree. (Molecular weight, 58.077.)

T, °K	C _p per gram	C _p per mole	T, °K	C _p per gram	C _p per mole
<i>Crystals</i>			<i>Liquid</i>		
81.3	0.2267	13.17	171.5	0.4471	25.97
86.0	.2379	13.82	177.3	.4528	26.30
91.2	.2506	14.55	187.8	.4602	26.73
97.3	.2649	15.38	193.5	.4664	27.09
102.5	.2776	16.12	202.7	.4733	27.49
104.8	.2872	16.68	208.5	.4779	27.75
<i>Liquid</i>			214.3	.4824	28.02
115.4	0.4085	23.72	225.0	.4917	28.56
122.1	.4122	23.94	230.6	.4973	28.88
136.5	.4239	24.62	240.2	.5065	29.42
142.8	.4270	24.80	245.4	.5127	29.78
154.6	.4345	25.23	253.0	.5231	30.38
160.8	.4402	25.57	258.3	.5283	30.68

⁵ K. K. Kelley, G. S. Parks and H. M. Huffman, J. Phys. Chem. 33, 1802 (1929).

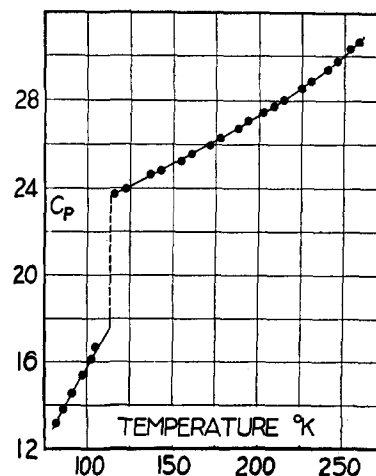


FIG. 1. The molal heat capacity of isobutane plotted against the absolute temperature.

ideal or "standard" curve for each class, such that at any temperature *T* the actual heat capacity (*C_p*) of a compound was reasonably well represented by the equation

$$C_p = (A + BT)C_p^\circ, \quad (1)$$

where *A* and *B* were empirical constants characteristic of the particular compound and *C_p*[°] was the heat capacity on the standard curve at the temperature in question. Accordingly the entropy of the compound at this particular temperature becomes simply

$$S_T = AS_T^\circ + B \int_0^T C_p^\circ dT, \quad (2)$$

where *S_T*[°] is the entropy increment corresponding to the standard curve from 0°K to *T* and $\int_0^T C_p^\circ dT$ is the increase in the standard heat content. To evaluate properly the empirical constants, *A* and *B*, it is simply necessary to substitute in Eq. (1) two reliable experimental values for *C_p* at different temperatures, such as 80° and 110°K.

Since 1929 this method has been extensively utilized in third law calculations for estimating

TABLE II. Fusion data for isobutane at 113.2°K.

	HEAT OF FUSION	
	cal./gram	cal./mole
First determination	18.50	1074.5
Second determination	18.53	1075.9
Mean	18.51	1075.2

the entropy increments of organic compounds in going from 0° to 80° or 90°K. However, only recently have experimental heat capacity data become available for further testing its applicability. The specific heat measurements of Giauque and Egan⁶ on carbon dioxide, of Bekkedahl and Matheson⁷ on "crystalline rubber hydrocarbon" (i.e., polymerized C₅H₈), of Aston and Messerly⁸ on tetramethylmethane, of Ahlberg, Blanchard and Lundberg⁹ on benzene, and of Southard and Brickwedde¹⁰ on naphthalene have now enabled us to make the comparisons given in Table III.

The "experimental S_{90} " values tabulated here were all obtained from the measured specific heats by graphical integration and the corresponding "calculated" values, except in the case of tetramethylmethane, were derived by Eq. (2) with the aid of the experimental heat capacities at 90° and 120°K. Tetramethylmethane, a rather unique organic compound, exhibits a transition of some sort in the neighborhood of 140°K and its measured specific heats appear to be more or less affected by this transition down even to about 75°. As a consequence its heat capacity curve for the crystals is far from standard and we have here estimated its entropy at 70° (instead of 90°) by employing its C_p value at 70° and assuming that in this case the value for B in Eq. (2) is zero.

From these comparisons of experimental and calculated entropies it is evident that the class II constants hold well for benzene and naphthalene and the class I constants for carbon dioxide. Such findings, of course, might have been anticipated from the earlier study of Kelley, Parks and Huffman. However, the class II curve also fits the data for the aliphatic isoprene unit very well and comes closer than the class I curve in giving an approximate result for tetramethylmethane. It thus appears probable that in entropy extrapolations the class II constants

TABLE III. *New tests of the extrapolation method for entropies. (Expressed in cal./degree per formula weight.)*

SUBSTANCE	EXPERIMENTAL VALUE OF S_{90}	CALCULATED			
		CLASS I		CLASS II	
		S_{90}	Error	S_{90}	Error
CO ₂ crystals	8.12	8.24	+0.12	9.33	+1.21
C ₅ H ₈ unit	8.37	7.47	-0.90	8.32	-0.05
C ₅ H ₁₂ *	12.02	9.50	-2.52	11.05	-0.97
C ₆ H ₆	10.89	9.97	-0.92	11.35	+0.46
C ₁₀ H ₈	13.52	11.27	-2.25	13.69	+0.17

* The data in this line apply at 70°K.

should be applied to all hydrocarbons,* whether aliphatic or cyclic, in preference to the class I constants, which probably apply solely to highly oxygenated or polar molecules.¹¹

This view is also supported by the fact that the experimental heat capacities for crystalline *n*-butane between 67° and 100°K fit the standard class II curve very closely, with values for $A=0.973$ and $B=0.00071$. The corresponding entropy extrapolation below 67°K yields 9.88 e.u. per mole, a result which would be good to ± 0.86 e.u. even if the extrapolation method should be in error here by as large a percentage as in the case of the highly anomalous tetramethylmethane.

By a similar extrapolation with the class II constants we have found 10.52 e.u. per mole for the increment in entropy of crystalline isobutane between 0° and 79°K. Here again our experimental heat capacities conform to Eq. (2) with remarkable fidelity. In spite of this fact, however, we feel that isobutane, closely related structurally to tetramethylmethane, may show at temperatures below 79°K a somewhat similar

* Note added to the proof.—Since the preparation of this manuscript R. K. Witt and J. D. Kemp [J. Am. Chem. Soc. 59, 273 (1937)] have published heat capacity values for crystalline ethane between 15° and the melting point, 89.87°K. Their data fit the class II curve quite well from 80° to 40° and yield, with the class II constants, a "calculated" entropy of 11.14 e.u. at 89.87°K. The corresponding experimental result is 10.74 e. u., a difference of 0.40 e. u.

¹¹ It should be noted here that the class I constants have been previously employed in this laboratory in all entropy extrapolations for aliphatic hydrocarbons. Accordingly, such entropies are not strictly comparable with those which are to be presented now for the two butanes; and for proper comparison these earlier extrapolations below 80° or 90°K will have to be revised upwards (by an average of perhaps 10 percent) with the aid of the class II constants.

⁶ W. F. Giauque and C. J. Egan, J. Chem. Phys. 5, 45 (1937).

⁷ N. Bekkedahl and H. Matheson, Nat. Bur. Stand. J. Research 15, 503 (1935).

⁸ J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. 58, 2354 (1936).

⁹ Ahlberg, Blanchard and Lundberg, J. Chem. Phys. (to be published); also referred to by Lord and Andrews, J. Phys. Chem. 41, 156 (1937).

¹⁰ J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc. 55, 4378 (1933).

TABLE IV. *The entropy of n-butane from calorimetric data (in calories per degree per mole).*

0°–67°K, Extrapolation (method of K. P. and H.)	9.88±0.7
67°–134.1°K, Crystals (graphical)	16.23
Fusion 1044.3/134.1	7.79
134.1°–272.5°K, Liquid (graphical)	20.25
Vaporization 5324/272.5	19.54±0.2
272.5°–298.1°K, Gas (average $C_p = 21.6$)	1.95
Correction for gas imperfection	0.14
Entropy of ideal gas at 1 atmos. and 298.1°K	75.8±0.8

positive deviation from our extrapolation formulas. In such an event this estimate of $S_{79} = 10.52$ e.u. may possibly be about one entropy unit too small.

The entropy of *n*-butane

With the aid of the extrapolation result given in the preceding section we have now recalculated the molal entropy of *n*-butane as an ideal gas at 298.1°K and 1 atmos. fugacity. The essential data are given in Table IV.

The entropy increments between 67° and 272.5°K have been obtained directly from the heat capacity data of Huffman, Parks and Barmore² for the crystalline and liquid states. These data have been carefully rechecked and the specific heat values above 220° slightly altered, since we have recently found that this laboratory's earlier specific heat determinations on hydrocarbons between 220° and 300°K were over-corrected (by a fraction of 1 percent) for certain radiation losses.

The entropy of vaporization (20.44 e.u.) adopted previously by Huffman, Parks and Barmore was undoubtedly too large. It was obtained by use of Burrell and Robertson's¹² approximate value for the heat of vaporization, which had been calculated from vapor pressure data by assuming perfect gas behavior of *n*-butane vapor and neglecting the volume of the liquid in the Clausius equation. By taking into account gas imperfection and the liquid volume, we now estimate $\Delta S = 19.60 (\pm 0.3)$ e.u. from Burrell and Robertson's data. However, the direct calorimetric determination of Dana, Jenkins, Burdick and Timm¹³ for the heat of

¹² G. A. Burrell and I. W. Robertson, J. Am. Chem. Soc. **37**, 2188 (1915).

¹³ L. I. Dana, A. C. Jenkins, J. N. Burdick and R. C. Timm, Refrigerating Eng. **12**, 387 (1926).

TABLE V. *The entropy of isobutane from calorimetric data (in calories per degree per mole).*

0°–79°K, Extrapolation (method of K. P. and H.)	10.52±1.0
79°–113.2°K, Crystals (graphical)	5.43
Fusion 1075.2/113.2	9.50
113.2°–260.9°K, Liquid (graphical)	22.05
Vaporization 5095/260.9	19.53±0.2
260.9°–298.1°K, Gas (average $C_p = 21.3$)	2.84
Correction for gas imperfection	0.12
Entropy of ideal gas at 1 atmos. and 298.1°K	70.0±1.1

vaporization of this substance is much more reliable. Adoption of their value for this heat effect and for the boiling point gives us the tabulated entropy of vaporization. It is undoubtedly very near the truth, since Aston and Messerly⁸ have recently found 19.24 e.u. for the vaporization entropy of tetramethylmethane and the data of Sage, Lacey and Schaafsma¹⁴ yield 19.61 e.u. for *n*-pentane.

The small entropy correction for gas imperfection has been made with Berthelot's equation according to the method of Giauque and Wiebe.¹⁵ The tabulated increment for gaseous butane between 272.5° and 298.1°K has been calculated on the assumption of a constant C_p of 21.6 cal. per mole, this being the value indicated for the mean temperature (285.3°K) in Fig. 36 of Sage and Lacey's recent paper.¹⁶

Considering the various sources of error in this third law calculation, we believe that our final value of $S_{298} = 75.8 \pm 0.8$ e.u. probably errs on the side of being a trifle high.

The entropy of isobutane

The essential contributions in the calculation of the entropy of isobutane by the third law are summarized in Table V. The increment for the crystals between 79° and 113.2°, the entropy of fusion and the increment for the liquid up to 260.9°K have been derived directly from the heat capacity data presented in the present paper. The entropy of vaporization has been obtained by use of the boiling point and corresponding heat of vaporization of isobutane reported by Dana, Jenkins, Burdick and Timm.¹³

¹⁴ B. H. Sage, W. N. Lacey and J. G. Schaafsma, Ind. Eng. Chem. **27**, 48 (1935).

¹⁵ W. F. Giauque and R. Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).

¹⁶ B. H. Sage and W. N. Lacey, Ind. Eng. Chem. **27**, 1484 (1935).

The correction for gas imperfection has been calculated by the method of Giauque and Wiebe.¹⁵ The increment for the gas between 260.9° and 298.1° has been calculated by the assumption of a constant C_p of 21.3 cal. per mole for isobutane, an estimate which we derived from a consideration of Sage and Lacey's¹⁶ specific heat curve for gaseous *n*-butane. The final value $S_{298}^\circ = 70.0$ e.u. is possibly a little too low.

Conclusion

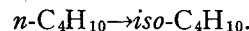
On the assumption of the third law of thermodynamics we have now calculated $S_{298}^\circ = 75.8 \pm 0.8$ e.u. for *n*-butane and $S_{298}^\circ = 70.0 \pm 1.1$ e.u. for isobutane. These values are lower than the corresponding ones calculated by Kassel¹ by 2.36 e.u. and 4.04 e.u., respectively; and the differences appear to be too great to be accounted for on the basis of errors in the thermal data or in the extrapolations from liquid-air temperatures down to the absolute zero.

A similar entropy discrepancy has been described by Kemp and Pitzer¹⁷ in the case of ethane and by Aston and Messerly⁸ in the case of tetramethylmethane. The situation, therefore, is apparently a general one and indicates that there is some fundamental error in either the third law or the statistical entropies. The difficulty may lie in an incorrect assumption of free rotation about the C—C bond in the statistical method, as already suggested by Kemp and Pitzer, or it may arise from the presence of a finite entropy at the absolute zero in all these crystalline hydrocarbons, as suggested by Kassel.

¹⁷ J. D. Kemp and K. S. Pitzer, J. Chem. Phys. **4**, 749 (1936).

THE ISOMERIZATION OF *n*-BUTANE

We are now in a position to consider the thermodynamics of the isomerization reaction



Rossini¹⁸ from his extremely accurate combustion data has calculated $\Delta H_{298}^\circ = -1630 (\pm 150)$ cal. for this reaction and our present entropy values yield $\Delta S_{298}^\circ = -5.8 (\pm 1.2)$ e.u. Hence, $\Delta F_{298}^\circ = -1630 + (298.1)(5.8) = 100 (\pm 400)$ cal. Thus at room temperature the *n*-butane is, perhaps, very slightly more stable than the *iso* compound.

At elevated temperatures, however, the comparative stability of the normal compound is probably much more pronounced. As Beeck¹⁹ has recently indicated the heat capacities of these two hydrocarbons in the gaseous state must be almost identical. Hence, the general free energy equation for this isomerization reaction becomes

$$\Delta F^\circ = -1630 + 5.8T. \quad (3)$$

Thus at 800°K (i.e., 527°C) $\Delta F^\circ = 3010$ cal. and an equilibrium mixture of the two butanes should contain 87 percent of the normal and 13 percent of the *iso* compound.

ACKNOWLEDGMENT

Before concluding, we wish to take this opportunity to thank the Shell Development Company and the Standard Oil Company of California for financial assistance in this investigation.

¹⁸ F. D. Rossini, J. Chem. Phys. **3**, 438 (1935).

¹⁹ O. Beeck, J. Chem. Phys. **4**, 680 (1936).