

TABLE IX

2-METHYL-2-BUTENE

Entropy, cal./deg./mole

T , °K.	289.90	298.16	311.73
Calorimetric value	80.19	80.90	82.04
Calculated ^a	80.22	80.92	82.05

Vapor Heat Capacity, cal./deg./mole

T , °K.	319.04	362.37	402.26	436.18	471.09
Calorimetric value	26.53	29.39	32.01	34.19	36.34
Calculated ^a	26.50	29.42	32.07	34.24	36.37

^a For effective barrier heights for methyl rotations of 450, zero, and 2350 cal./mole.

Table X lists values of the free-energy function, heat-content function, entropy, and heat capacity of 2-methyl-2-butene vapor at selected temperatures up to 1500°K. These were calculated using the moments of inertia, vibrational frequencies, and barrier heights given previously.

TABLE X

THERMODYNAMIC FUNCTIONS OF 2-METHYL-2-BUTENE

T , °K.	$(H_0^\circ - F_T^\circ)/$		S_T° , cal./deg./ mole	C_{pT}° , cal./deg./ mole
	T , cal./deg./ mole	$H_T^\circ - H_0^\circ$ kcal./mole		
298.16	64.71	4.833	80.92	25.10
300	64.79	4.878	81.05	25.22
400	69.87	7.736	89.21	31.93
500	74.53	11.25	97.02	38.07
600	78.89	15.32	104.43	43.42
700	83.06	19.90	111.49	48.04
800	87.03	24.91	118.17	52.05
900	90.85	30.29	124.50	55.52
1000	94.52	36.00	130.52	58.55
1100	98.06	41.99	136.23	61.16
1200	101.46	48.22	141.64	63.45
1300	104.75	54.67	146.80	65.42
1400	107.91	61.31	151.70	67.14
1500	110.99	68.10	156.39	68.63

The entries in the table are internally consistent to the number of significant figures given, but the actual uncertainty in the values may be several tenths of a unit at the higher temperatures.

Rotational Tautomers of 2-Methyl-1-butene.

—The molecule of 2-methyl-1-butene can exist in two tautomeric forms which differ with respect to the angle of rotation of the ethyl group. The complexity of the spectra of this compound indicates that both forms are present in appreciable amounts at ordinary temperatures. If it were known to which of the two forms each observed vibrational frequency corresponds (as could be ascertained by studying the relative intensities of the Raman lines as a function of temperature) it might be possible to make vibrational assignments for both forms and then use the calorimetric data reported here to obtain information about the energy difference between the two forms.

Acknowledgment.—Thanks are tendered to Wf. Roberts, formerly of this station, for his assistance with some of the measurements.

Summary

The following thermodynamic properties were determined for 1-pentene, 2-methyl-1-butene, and 2-methyl-2-butene: heats of vaporization at three temperatures, vapor heat capacities at five temperatures, vapor pressures and normal boiling points, second virial coefficients, values of $(\partial C_p/\partial P)_T$, and the entropies of the vapors at three temperatures.

A vibrational assignment was made for 2-methyl-2-butene, and the free energy function, heat content function, entropy and heat capacity of this substance were computed for selected temperatures up to 1500°K. by statistical mechanical methods.

BARTLESVILLE, OKLA.

RECEIVED MARCH 3, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXIV. The Heat Capacities, Entropies and Free Energies of *cis*- and *trans*-Decahydronaphthalene¹

BY GEORGE S. PARKS AND JOHN A. HATTON

A comprehensive study of the physical-chemical properties of *cis*- and *trans*-decahydronaphthalene was initiated about twelve years ago by Professor W. F. Seyer² of the University of British Columbia. With the aid of several students he prepared these compounds in rather pure form and measured their freezing points, densities, refractive indices, surface tensions, viscosities, vapor

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the San Francisco Meeting, March, 1949.

(2) W. F. Seyer and co-workers, *THIS JOURNAL*, **60**, 2125 (1938); **63**, 2425 (1941); **64**, 1912 (1942); **67**, 328 (1945); **70**, 802 (1948).

pressures and dielectric constants. In 1940 he also gave samples of his purified materials to Professor E. C. Gilbert of Oregon State College for the accurate measurement of the heats of combustion³ and to one of us (G. S. P.) for the determination of the heat capacities at low temperatures. While we completed these last measurements in 1941, the publication of the results has been delayed by various wartime and post-war exigencies.

In the present paper we shall present compara-

(3) G. F. Davies and E. C. Gilbert, *ibid.*, **63**, 1585 (1941).

tive data for the heat capacities, entropies and free energies of the two isomers.

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 other places.⁴ In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is ordinarily less than 0.7%, except insofar as impurities in a sample may cause premelting at the upper temperatures of the crystals. The fortuitous errors are usually under 0.25%; and this latter figure may also be considered our probable *relative* error in making comparisons between these two isomers.

From the amount of premelting in the fusion determinations we have estimated the purity of the *cis*-isomer as 99.6 mole % and that of the *trans* as 98.9 mole %.

In all, seventy-six specific heat determinations in the temperature interval between 78 and 298° K. were made on the two isomers. The results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read off from this curve for various even temperatures. For the sake of spatial economy and ease of comparison these derived values, rather than the more numerous experimental ones, are recorded in Table I. They and also the fusion data of Table II are expressed in terms of the *defined* conventional calorie⁵ and with all weights reduced to a vacuum basis.

The experimental values for the specific heats, however, are represented graphically in Fig. 1.

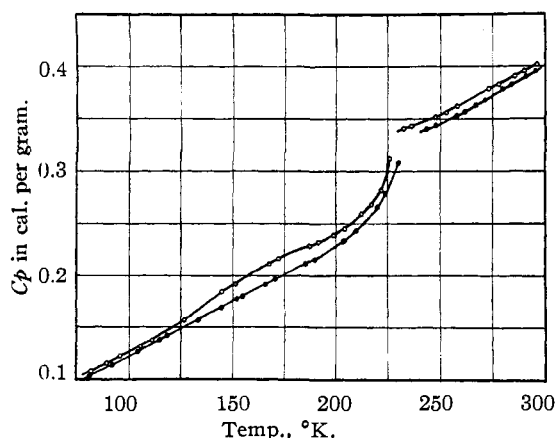


Fig. 1.—The specific heat curves for the decahydronaphthalenes; the upper curves with circles refer to the *cis*- and the lower curves with dots to the *trans*-isomer.

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

(5) The factor 1/4.1833 has been used in converting the international joule to the defined calorie.

TABLE I
SPECIFIC HEATS (C_p) IN CALORIES PER GRAM OF THE
DECAHYDRONAPHTHALENES

T , °K.	<i>cis</i>	<i>trans</i>	T , °K.	<i>cis</i>	<i>trans</i>
80	0.1070 c	0.1020 c	200	0.2408	0.2297
90	.1167	.1122	210	.2546	.245
100	.1267	.1224	220	.277 c	.266
110	.1370	.1328	230	.3390 l	.309 c
120	.1480	.1432	240	.3459	.3376 l
130	.1610	.1536	250	.3536	.3458
140	.1760	.1640	260	.3640	.3553
150	.1904	.1744	270	.3753	.3664
160	.2035	.1848	280	.3861	.3783
170	.2140	.1953	290	.3960	.3903
180	.2225	.2057	298.16	.4040 l ^a	.3997 l ^a
190	.2310	.2163			

^a c = crystalline; l = liquid; 273.16°K. = 0°C.

TABLE II
FUSION DATA^a FOR THE DECAHYDRONAPHTHALENES

Substance	M. p., °K.	Heat of fusion (cal. per g.)		
		I	II	Mean
<i>cis</i> -Isomer	230.1	16.96	16.98	16.97
<i>trans</i> -Isomer	242.4	24.91	24.93	24.92

^a In the calculation of these fusion values, the somewhat more rapid rise in the specific heat of the crystals 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.

Here the results for the crystals of the *cis*-isomer exhibit a rather unusual upward bulge in the 140–190° temperature interval. We have no satisfactory explanation for this phenomenon but its reality, at least as far as our sample was concerned, was checked by a subsequent set of measurements which Dr. M. L. Renquist made in This Laboratory with a "semi-micro" calorimeter.

Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.16°K. for the two isomers. The detailed entropy values are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman⁶ for estimating the entropy increases for the crystals from 0 to 80°K. The various incre-

TABLE III
ENTROPIES OF THE DECAHYDRONAPHTHALENES (IN CALORIES PER DEGREE PER MOLE)

	<i>cis</i>	<i>trans</i>
Crystals (0–80°)	12.69	11.84
Crystals (80°, m. p.)	25.73	26.20
Fusion	10.20	14.21
Liquid (m. p. –298.16°)	13.18	10.49
S_{298}^0 for the liquid state	61.80	62.74

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

ments from 80 to 298.16°K., which appear in the next three lines, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree per mole are then given in the last line with the designation " S_{298}^0 "; they are probably reliable to within 0.7 e. u. in an absolute sense and to 0.3 e. u. for comparative purposes.

Free Energy Data for the Decahydronaphthalenes

We have also calculated the free energies of formation of these isomers in the liquid state by means of the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The essential thermal data are listed in Table IV.

TABLE IV

THERMAL DATA AT 298.16°K. FOR THE DECAHYDRO-NAPHTHALENE ISOMERS IN CALORIES PER MOLE; MOL. WT., 138.244

	<i>cis</i>	<i>trans</i>
ΔH_f^0 of liquid	-52,440	-54,560
ΔS_f^0 of liquid	-232.71	-231.77
ΔF_f^0 of liquid	16,940	14,550
ΔF_v^0 of vaporization	3,470	3,010
ΔF_g^0 of gas	20,410	17,560

The values for the ΔH^0 of formation of the liquid compounds were obtained by a revision of the combustion data of Davies and Gilbert³ in terms of present-day standards,⁷ and the use of 68,317.4 cal. and 94,051.8 cal.⁸ for the heats of formation of water and carbon dioxide, respectively. The ΔS_f^0 values represent simply the differences between the S_{298}^0 for each isomer and the corresponding values for the entropies of the elements

(7) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(8) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *ibid.*, **34**, 143 (1945).

contained therein. For this purpose we have used 31.211 e. u. for the entropy of hydrogen and 1.361 e.u. for carbon (β -graphite).⁸ The resulting molal free energies for the liquids are probably reliable to ≈ 400 calories in an absolute sense and to about one-half of this figure for the present comparative purposes.

The free energy changes for the vaporization of each liquid at 298.16°K. to yield a gas at the hypothetical fugacity of 1 atm. have been calculated by use of 2.19 and 4.73 mm. for the respective vapor pressures of the *cis*- and *trans*-compounds. These are values which we have deduced from a plot of Seyer's vapor pressure data.² Addition of the ΔF^0 of vaporization quantities to the free energies of the liquids then gives the tabulated free energies of formation for the gaseous state.

These data now yield for the free energy changes in the isomerization process

$$cis\ C_{10}H_{18} \longrightarrow trans\ C_{10}H_{18}$$

$$\Delta F_{298}^0 \text{ (in liquid phase)} = -2390 (\approx 280) \text{ cal.}$$

and

$$\Delta F_{298}^0 \text{ (in gas phase)} = -2850 (\approx 280) \text{ cal.}$$

Summary

1. The specific heats of *cis*- and *trans*-decahydronaphthalene have been measured between 78 and 298°K. The corresponding heats of fusion also have been measured.

2. The entropies (*cis*, 61.80 \pm 0.7 e.u. and *trans*, 62.74 \pm 0.7 e.u.) of these two isomers in the liquid state at 298.16°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies for both the liquid and gaseous states have then been calculated from these entropies and other available data.

STANFORD, CALIFORNIA

RECEIVED MARCH 22, 1949

[CONTRIBUTION NO. 709 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heats of Formation of Sodium Borohydride, Lithium Borohydride and Lithium Aluminum Hydride^{1,2}

BY WILLIAM D. DAVIS,³ L. S. MASON AND G. STEGEMAN

A number of metallo-borohydrides of the general formula $M(BH_4)_x$ and a number of metallic hydrides of unusual interest have been prepared and studied.⁴ Reviews of the chemistry⁵ and of the

(1) This study is a part of a research project sponsored by the Office of Naval Research.

(2) This report is part of a thesis presented by William D. Davis in partial fulfillment of requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Pittsburgh, January, 1949.

(3) Present address: Knolls Atomic Power Laboratory, The General Electric Corporation, Schenectady, New York.

(4) (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *THIS JOURNAL*, **62**, 3421 (1940). (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940). (c) H. I. Schlesinger and H. C. Brown, *ibid.*,

physical properties and structures^{6,7} of the hydrides of boron and their derivatives have been published. Thermochemical information about these substances, however, is meager and in some cases uncertain. In the present study, the heats of formation of sodium borohydride, lithium borohydride, and lithium aluminum hydride have been determined by measuring calorimetrically the

62, 3429 (1940). (d) H. I. Schlesinger, H. C. Brown and G. W. Schaeffer, *ibid.*, **65**, 1786 (1943). (e) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

(5) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(6) S. H. Bauer, *ibid.*, **31**, 43 (1942).

(7) J. W. Smith, *Science Progress*, **35**, No. 139, 515 (1947).