

2. Dehydrogenation and aromatization of normal heptane is the predominant set of reactions up to 525°.

3. Conditions for revivification of spent chromium oxide gel catalyst have been defined.

4. Water acts as a transient poison for the dehydrogenation activity of the gel catalyst.

5. Transitions from black to green forms of

chromium oxide gel catalyst have been found to represent states of oxidation of the catalyst and not active and inactive forms for the dehydrogenation and aromatization of liquid paraffins.

6. The glow phenomenon carried out in a non-oxidizing atmosphere, as in hydrogen or nitrogen, does not affect activity of the chromium oxide gel.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXI. Some Heat Capacity, Entropy and Free Energy Data for the Four Methylnonanes

BY GEORGE S. PARKS, THEO J. WEST AND GEORGE E. MOORE

The preparations and some physical properties of the four isomeric methylnonanes have been described by Calingaert and Soroos.¹ After the completion of their work, these investigators kindly loaned us samples of the compounds for our present study of the heat capacities at low temperatures and important thermodynamic properties derived therefrom.

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.² 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%, except insofar as impurities in a sample may cause premelting at the upper temperatures of the crystals. The fortuitous errors were ordinarily under 0.25%; and this latter figure may also be considered our probable *relative* error in making comparisons among the decane isomers.

On an average about forty specific heat determinations in the temperature interval between 80 and 298°K. were made upon each of the methylnonanes. These 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 calorie³ and with all weights reduced to a vacuum basis.

From the amount of premelting in the various fusion determinations we have obtained the following estimates of the purity of the compounds in mole %: 2-methyl, 99.1; 3-methyl, 99.7; 4-methyl, 99.3; and 5-methyl, 99.7.

Two of these methylnonanes, the 3-methyl and 4-methyl compounds, contain an asymmetric carbon atom and in these cases our liquid samples were really equimolar mixtures of the dextro and levo forms. On crystallization at low temperatures these liquids probably produce, like *d-l*-pinene,⁴ a eutectic mixture of the *d* and *l* isomers. On this assumption we have estimated, with the aid of the data in Table II, that the freezing points of the pure 3-methyl and 4-methyl isomerides would really come at about 199 and 186°K., respectively.

With rather rapid cooling to the temperature of liquid air, the 4-methyl compound could be obtained readily as a glass; and we were able to make a series of measurements of the heat capacity of this undercooled, amorphous material. These results were similar to those obtained previously by the Nernst method with other glassy substances.⁵ In this case they exhibit a sudden 75% rise in the temperature interval 109–122°. The specific heat values thus derived for the glass at the several even temperatures of the tabulation are given in the right branch of the fourth column

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

(4) Ross and Somerville, *J. Chem. Soc.*, 2770 (1926).

(5) Parks, Thomas and Light, *J. Chem. Phys.*, 4, 64 (1936).

(1) Calingaert and Soroos, *THIS JOURNAL*, 58, 635 (1936).

(2) Parks, *ibid.*, 47, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, 30, 47 (1926).

of Table I, by the side of the values for the corresponding crystals.

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

(c = crystalline; l = liquid; a = amorphous; 273.16°K. = 0°C.)

T , °K.	2-Methyl- nonane	3-Methyl- nonane	4-Methyl- nonane	5-Methyl- nonane
80	0.1757 c	0.1691 c	0.1732 c	0.1810 a
90	.1909	.1848	.1891	.1991
100	.2063	.2000	.2052	.2175
110	.2211	.2146	.2211	.254
120	.2350	.2285	.2349	.427
130	.2475	.2425	.2470	.438
140	.2600	.2563	.2598	.438 a
150	.2724	.2688	.2745	...
160	.2848	.2803	.325 c	...
170	.3020	.29793075
180	.343	.340 c	0.4440 l	.360 c
190	.464 c	.4426 l	.4450	.4448 l
200	.4680 l	.4477	.4510	.4491
210	.4688	.4530	.4570	.4544
220	.4705	.4580	.4630	.4599
230	.4738	.4632	.4690	.4663
240	.4782	.4694	.4758	.4739
250	.4849	.4766	.4844	.4815
260	.4922	.4850	.4938	.4898
270	.5003	.4939	.5029	.4994
280	.5095	.5030	.5126	.5090
290	.5186	.5119	.5240	.5187
298	.5263 l	.5190 l	.5331 l	.5282 l

TABLE II
FUSION DATA^a

Substance	M. p., °K.	Heat of fusion (cal. per g.)		
		I	II	Mean
2-Methylnonane	198.8	29.39	29.38	29.38
3-Methylnonane	188.5	31.55	31.28	31.41
4-Methylnonane	174.7	25.59	25.43	25.51
5-Methylnonane	186.7	27.93	27.97	27.95

^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.

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 these four substances. 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 (Column 2) from 0 to 80°K.

(6) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

The various increments from 80 to 298.16°K., which appear in the next three columns, 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 sixth column under the heading " S_{298}° "; they are probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes. These experimental values for the two liquids which contain dextro and levo forms in equal amounts presumably include a contribution for the entropy of mixing, equal to $R \ln 2$. Subtraction of this quantity then gives the values tabulated for the pure d or l isomerides.

The heat capacity of n -decane has been previously studied by Huffman, Parks and Barmore.⁷ Its value for S_{298}° , revised and corrected for the present molecular weight, is 102.7 e. u. Subtraction of this quantity from the entropies just found for the methylnonanes then gives the ΔS values, in the last column of Table III, for the isomerization of n -decane to the respective compounds. They average -2.0 e. u., which is considerably less than the effect (-4.5 e. u.) previously deduced by Parks and Huffman⁸ mainly from a study of hydrocarbons with multiple branching.

Free Energy Data for Three Decanes

We have also calculated the free energies of formation of the 2-methyl- and 5-methylnonane 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.

The values for the ΔH_{298}° of formation of these two hydrocarbons were obtained from the combustion study of Moore, Renquist and Parks.⁹ They have been subjected to a slight revision for the recent change in the atomic weight of hydrogen.¹⁰ The ΔS_{298}° values represent simply the differences between the S_{298}° for each methylnonane and the corresponding values for the entropies of the elements contained therein. For this purpose we have used 15.615 e. u.¹¹ for the entropy of $1/2$ H_2 and 1.36 e. u.¹² for C (β -graphite). The molal free energies appear in the last column

(7) Huffman, Parks and Barmore, *THIS JOURNAL*, **53**, 3786 (1931).

(8) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, N. Y., 1932, p. 70.

(9) Moore, Renquist and Parks, *THIS JOURNAL*, **62**, 1505 (1940).

(10) Baxter, Guichard, Hönigschmid and Whytlaw-Gray, *ibid.*, **62**, 669 (1940).

(11) Giauque, *ibid.*, **52**, 4825 (1930).

(12) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

TABLE III
ENTROPIES OF THE LIQUID METHYLNONANES PER MOLE
Molecular weight: 142.276

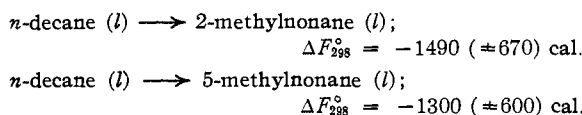
Substance	Crystals		Fusion	Liquid	S_{298}°	ΔS isomerization
	0-80°K.	Above 80°K.				
2-Methylnonane	19.46	31.86	21.04	28.07	100.4	-2.3
<i>d-l</i> ,3-Methylnonane	18.57	28.72	23.72	31.05	102.1	
3-Methylnonane, pure <i>d</i> or <i>l</i>					100.7	-2.0
<i>d-l</i> ,4-Methylnonane	18.88	25.95	20.79	36.06	101.7	
4-Methylnonane, pure <i>d</i> or <i>l</i>					100.3	-2.4
5-Methylnonane	19.38	28.96	21.30	31.67	101.3	-1.4

TABLE IV
THERMAL DATA AT 298.16°K. FOR THREE DECANES
In calories per mole. Molecular wt. 142.276

Substance	ΔH_{298}° , cal.	ΔS_{298}° , e. u.	ΔF_{298}° , cal.
<i>n</i> -Decane (<i>l</i>)	-72,370	-254.4	3480
2-Methylnonane (<i>l</i>)	-74,550	-256.7	1990
5-Methylnonane (<i>l</i>)	-74,090	-255.8	2180

of the table. In view of the accuracy of the contributing data, the uncertainty in these values is probably within 600 calories.

Similar data for *n*-decane, taken from a previous study by Parks,¹³ also have been included in Table IV for the purpose of comparison. Thus we find for the two isomerizations



(13) Parks, *Chem. Rev.*, **27**, 75 (1940).

This slightly greater stability, at room temperature, of the branched isomers as compared with the normal hydrocarbon is in general accord with the free energy data published recently by Rossini and Prosen¹⁴ for the isomeric hexanes.

Summary

1. The specific heats of the four methylnonanes have been measured between 80 and 298°K. The corresponding heats of fusion also have been determined.

2. The entropies of these hydrocarbons in the liquid state at 298.16°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies of the 2-methyl- and 5-methylnonane also have been calculated. These are lower than the free energy of *n*-decane by 1490 and 1300 cal., respectively.

(14) Rossini and Prosen, *This Journal*, **62**, 2250 (1940).

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The Vapor Density of Hydrazine

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In connection with their measurements of the heat capacity of gases by the hot wire method Eucken and Krome^{1a} reported recently that hydrazine vapor is largely associated according to the equation $2N_2H_4 \rightleftharpoons N_4H_8$. They stated that a vapor density determination by the Dumas method indicated complete association at 105.8° and 340 mm. They also measured the dissociation constant, which they give as $\log K_p = 8.68 - 3060/T$ (pressure in mm.). From this the heat of dimerization was estimated to be 14.0 kcal./mole. These results seemed to us surprising as

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(1a) A. Eucken and H. Krome, *Z. physik. Chem.*, **B45**, 175 (1940).

they are not to be expected from the structure of hydrazine or from analogy with closely related compounds. Furthermore, in the course of molecular structure investigations carried out some time ago in these Laboratories a number of electron-diffraction photographs of hydrazine vapor were obtained, of which none revealed the presence of double molecules. Since no other reference to this matter could be found in the literature, we decided to redetermine vapor density at various temperatures and pressures. The results reported here show that gaseous hydrazine is not associated to any appreciable extent.

The hydrazine used was prepared by repeatedly