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HEATS OF ISOMERIZATION OF THE 18 OCTANES

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ABSTRACT

The heats of isomerization of all of the 18 octanes were determined by measurement of the ratios of their heats of combustion, in the liquid state for 17 and the solid state for 1, using the procedure previously described for the hexanes and the heptanes.

Values of the heats of isomerization are reported for the condensed (liquid or solid) state at 25° C and for the gaseous state at 25° C and 0° K.

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I. INTRODUCTION

In continuation of the program of determining the heats of formation and of isomerization of the paraffin hydrocarbons [1, 2, 3, 4]¹, calorimetric measurements have been made which yield values for the differences in the heats of combustion of all of the 18 octanes at 25° C. These values for the differences in the heats of combustion, which, for the same state, are also the heats of isomerization at 25° C, have been combined with heats of vaporization (or sublimation for the one solid octane), measured by Osborne and Ginnings [5], to give values for the heats of isomerization in the gaseous state at 25° C. Combination of these with values for the decrease in heat content of the various isomers in the gaseous state from 25° C to 0° K, calculated by Pitzer [6], gives values for the energies of isomerization for the ideal gaseous state at 0° K.

¹ Figures in brackets indicate the literature references at the end of this paper. References to the earlier papers are given in [1].

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the international joule. For conversion to the conventional thermochemical calorie, the following relation is used [7]:

$$4.1833 \text{ international joules (NBS)} = 1 \text{ calorie.}$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010 from the 1941 table of atomic weights [8].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [9].

Definitions of all symbols used are given in a previous paper [2].

III. METHOD AND APPARATUS

The same method and apparatus were used in the present investigation as in the work on the hexanes [2] and heptanes [3].

IV. EXPERIMENTAL PROCEDURES

1. CHEMICAL PROCEDURE

The description of the octanes investigated is summarized in table 1, which gives the name of the compound, the normal state (liquid or solid) at 25° C, the source of the material, and, where known, the amount of impurity. For 13 of the octanes, determination of the amount of impurity was made by A. R. Glasgow, Jr., of the American Petroleum Institute Research Project 6 at this Bureau, from time-temperature freezing and melting curves [19]. For the others, estimates of the amount of impurity were made by the authors, considering the method of purification and the purity of related isomers. The octanes used were so prepared and purified that the residual impurities must have consisted largely of isomeric octanes. Further, the impurities would be largely only those isomers having boiling points near that of the given isomer. The values given in table 2 indicate the tolerances with regard to such impurities, and also the actual estimated amounts of impurity. From these data, it appears that the amounts of impurity in the 18 octanes were not sufficient to affect their heats of combustion significantly, with the possible exception of 2,3-dimethylhexane.

The procedures for sealing the liquid hydrocarbons in glass ampoules, purifying the oxygen used for combustion, igniting the hydrocarbon, examining the products of combustion, and determining the amount of reaction have been described previously [2].

TABLE 1.—Source and purity of the octanes investigated

Compound	State	Source ^a	Amount of impurity
<i>n</i> -Octane (I).....	Liquid.....	A	<i>Mole fraction</i> 0.0080±0.0010
<i>n</i> -Octane (II).....	do.....	A	.0035±0.0005
2-Methylheptane.....	do.....	A	<.03
3-Methylheptane.....	do.....	A	<.03
4-Methylheptane.....	do.....	A	<.015
3-Ethylhexane.....	do.....	A	b(<.02)
2,2-Dimethylhexane.....	do.....	A, B	<.015
2,3-Dimethylhexane.....	do.....	A, B	b(<.05?)
2,4-Dimethylhexane.....	do.....	A, B	b(<.02)
2,5-Dimethylhexane.....	do.....	A, B	<.01
3,3-Dimethylhexane.....	do.....	A, B	<.005
3,4-Dimethylhexane.....	do.....	A, B	b(<.02)
2-Methyl-3-ethylpentane.....	do.....	A	<.01
3-Methyl-3-ethylpentane.....	do.....	A, B	<.006
2,2,3-Trimethylpentane.....	do.....	A, B	<.005
2,2,4-Trimethylpentane.....	do.....	C	<.002
2,3,3-Trimethylpentane.....	do.....	A, B	<.01
2,3,4-Trimethylpentane.....	do.....	A	<.005
2,2,3,3-Tetramethylbutane.....	Solid.....	D	b(<.02)

^a The letters in this column have the following significance:

- A, Prepared by the American Petroleum Institute Hydrocarbon Research Project at the Ohio State University. These materials were made available by Cecil E. Boord, Supervisor of the Project, and George Calingaert, Chairman of the Subcommittee on Physical Properties.
- B, Further purified by the American Petroleum Institute Research Project 6 at the National Bureau of Standards by means of azeotropic distillation in columns of high efficiency (approximately 100 theoretical plates) at a high reflux ratio (100 to 1);
- C, purified from relatively pure 2,2,4-trimethylpentane prepared commercially (Rohm and Hass Company, Philadelphia, Pa.) by azeotropic distillation (as under B), by the American Petroleum Institute Research Project 6;
- D, purified by crystallization by A. R. Glasgow, Jr., of the American Petroleum Institute Research Project 6, from material prepared by the Chemical Research Laboratory of the Ethyl Corporation, Detroit, Mich. This material was made available by George Calingaert, Director of Chemical Research of the Ethyl Corporation.

^b Estimated; see text.

For the combustion of the solid 2,2,3,3-tetramethylbutane, glass ampoules could not be used, and, since the sample was required to be inclosed because of its volatility, gelatin capsules were used for the purpose. All the capsules were from one lot of No. 000 gelatin capsules.² These were dried by heating in an oven at 100° C, cooled in a desiccator, and weighed in small closed bottles out of contact with the air of the room. A heating time of 6 to 8 hours usually served to bring the capsules to constant weight. For each combustion experiment involving a gelatin capsule as the inclosure for the main combustible material, the mass ("dry") of the gelatin capsule was first determined. Then the solid sample was packed into the capsule and the cover put on. The cover of the capsule was sealed to the body by dipping the entire capsule halfway under water for several seconds.

² From Sharp and Dohme, Baltimore, Md.

TABLE 2.—Tolerances of the amounts of close-boiling isomeric impurities in the octanes

Compound	Close-boiling isomers	Amount of each such impurity required to change the heat of combustion by five parts in 100,000	Amount of impurity in the material used in the present work
		Mole fraction	Mole fraction
<i>n</i> -Octane (I)			0.0080
<i>n</i> -Octane (II)			.0035
2-Methylheptane	3-Methylheptane	0.10	
	4-Methylheptane	.08	
	3-Ethylhexane	.06	< .03
3-Methylheptane	2-Methylheptane	.10	
	4-Methylheptane	.37	< .03
	3-Ethylhexane	.14	
4-Methylheptane	2-Methylheptane	.08	
	3-Methylheptane	.37	< .015
	3-Ethylhexane	.22	
3-Ethylhexane	2-Methylheptane	.06	
	3-Methylheptane	.14	a(< .02)
	4-Methylheptane	.22	
	3-Methyl-3-ethylpentane	.11	
2,2-Dimethylhexane	2,4-Dimethylhexane	.06	
	2,5-Dimethylhexane	.18	< .015
	2,2,3,3-Tetramethylbutane	.04	
	3,4-Dimethylhexane	.36	
2,3-Dimethylhexane	2-Methyl-3-ethylpentane	.09	a(0.05?)
	2,3,3-Trimethylpentane	.30	
2,4-Dimethylhexane	2,5-Dimethylhexane	.08	a(< .02)
2,5-Dimethylhexane	2,4-Dimethylhexane	.08	< .01
3,3-Dimethylhexane	2,3,3-Trimethylpentane	.07	
	2,3,4-Trimethylpentane	.11	< .005
3,4-Dimethylhexane	2-Methylheptane	.09	
	3-Methylheptane	.19	a(< .02)
	4-Methylheptane	> .5	
	3-Ethylhexane	.19	
	2,3-Dimethylhexane	.09	
2-Methyl-3-ethylpentane	3-Methyl-3-ethylpentane	.08	< .01
	2,3,3-Trimethylpentane	.07	
	3-Ethylhexane	.11	
3-Methyl-3-ethylpentane	3,4-Dimethylhexane	.27	< .006
	2-Methyl-3-ethylpentane	.08	
2,2,3-Trimethylpentane	2,4-Dimethylhexane	> .5	< .005
	2,5-Dimethylhexane	.08	< .002
2,2,4-Trimethylpentane	2,3,4-Trimethylpentane	.18	
2,3,3-Trimethylpentane	2,3-Dimethylhexane	.30	< .01
	3,3-Dimethylhexane	.11	
2,3,4-Trimethylpentane	2,3,3-Trimethylpentane	.18	< .005
2,2,3,3-Tetramethylbutane	2,2-Dimethylhexane	.04	
	2,2,4-Trimethylpentane	.03	a(< .02)

^aEstimated; see text.

For the solid octane, two types of experiments were performed. In the first type were measured the temperature rise of the calorimeter and the mass of carbon dioxide formed in the combustion of a mass (not accurately known) of 2,2,3,3-tetramethylbutane together with a known mass of gelatin capsule. In the second type of experiment were measured in one series, I, the temperature rise of the calorimeter and the mass of carbon dioxide formed in the combustion of a known mass of gelatin capsule, and in another series, II, the temperature rise of the calorimeter and the mass of carbon dioxide formed in the combustion of a known mass of gelatin capsule together with a known mass of pure benzoic acid of known heat of combustion. The second type of experiment served to determine the amount of heat and of carbon dioxide evolved in the combustion of unit mass of gelatin, the I series involving the determination directly on 13 capsules (1 capsule

in experiment No. 1, and 4 capsules each in experiments 2, 3, and 4 of table 4), and the II series involving the determination indirectly, but under conditions simulating more closely the combustion experiments, with two experiments (Nos. 5 and 6 of table 4) involving one capsule and a known standard amount of pure benzoic acid (NBS Standard Sample 39 e).

The average values obtained for the amount of heat evolved and the mass of carbon dioxide formed in the combustion of unit mass of gelatin capsule were combined with the data of the first type of experiment to obtain the temperature rise of the calorimeter and the mass of carbon dioxide formed from the combustion of the 2,2,3,3-tetramethylbutane alone.

2. CALORIMETRIC PROCEDURE

The calorimetric procedure was the same as that in the work on the hexanes [2] and heptanes [3].

V. RESULTS

The experimental results of the present investigation are presented in tables 3, 4, and 5, which give the data yielding values of B in ohms per gram of carbon dioxide, as defined by eq 4 of the paper on the hexanes [2], for 17 of the octanes in the liquid phase, and for the eighteenth octane (2,2,3,3-tetramethylbutane) in the solid phase, at 28° C. The symbols have the same significance as in previous reports [2, 12].

In the experiments on 2-methylheptane, there was a loss of carbon dioxide during the analysis of the products of combustion of the calorimetric combustion experiments. In order to save repeating the latter experiments, a series of four noncalorimetric combustion experiments was performed to determine the ratio of the mass of carbon dioxide formed to that calculated stoichiometrically from the mass of sample. These four experiments yielded the following value for this ratio: Mean, 0.99970; standard deviation of the mean, ± 0.00006 . The values of the mass of carbon dioxide formed as given in table 3 are calculated from the foregoing ratio. The uncertainty assigned to the final value for 2-methylheptane was increased by the uncertainty in the stoichiometric ratio.

In table 6 are given, for the 18 octanes, values of the following: The constant B in ohms per gram of carbon dioxide, as given in tables 3 and 5; the ratio of the heat evolved, per mole of hydrocarbon, in the bomb process at 28° C for each isomer to that for n -octane; the difference, between n -octane and each isomer, in the heat of combustion in the bomb process at 28° C; and the heat of isomerization of n -octane into each isomer, at 25° C and 1 atm, for the liquid state for the 17 normally liquid octanes and for the solid state for 2, 2, 3, 3-tetramethylbutane. The value of the heat of isomerization was obtained by means of the relation [2]

$$(-\Delta U_B)_n - (-\Delta U_B)_i = (-\Delta U_B)_n (1 - B_i/B_n).$$

For this calculation, the value of $(-\Delta U_B)_n$ at 28° C was taken as 5458.8 int. kj/mole [4].

TABLE 3.—Results of the calorimetric combustion experiments on the seventeen liquid octanes

Compound	Number of experiments ^a				Mass of carbon dioxide formed	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_c	Δr_i	Δr_n	<i>B</i> ^o	
	<i>A</i>	<i>B</i>	<i>C</i>	Total								Mean	Standard deviation of the mean
<i>n</i> -Octane		b 4	b 6	10	2.26440 to 2.87367 2.28907	0.001937 to .001957 .001932	0.000418 to .002160 .000853	0.000070 to .000365 .000024	0.255416 to .323369 .258272	0.000400 to .000421 .000529	0.000020 to .000098 .000063	0.1125810	±0.000062
2-Methylheptane		7		7	2.68633 2.32827	.001939 .001939	.002061 .000791	.000072 .000088	.303029 .261931	.000542 .000410	.000088 .000082	.1124730	.0000030
3-Methylheptane		3	3	6	2.61833 2.34562	.001953 .001938	.001857 .000979	.000125 .000077	.301352 .263945	.000424 .000398	.000089 .000077	.1125282	.0000050
4-Methylheptane			5	5	2.63248 2.22709	.001947 .001952	.001838 .001293	.000166 .000348	.296124 .251115	.000423 .000399	.000089 .000017	.1125434	.0000053
3-Ethylhexane			5	5	2.55087 2.17294	.001971 .001961	.002293 .002090	.000376 .000349	.287541 .244059	.000409 .000411	.000021 .000026	.1125690	.0000039
2,2-Dimethylhexane			4	4	2.25164 2.17520	.001973 .001950	.002518 .000202	.000406 .000315	.252910 .245209	.000421 .000382	.000030 .000019	.1123315	.0000025
2,3-Dimethylhexane			7	7	3.02957 2.00103	.001974 .001959	.002509 .001449	.000382 .000367	.341297 .225384	.000417 .000380	.000042 .000020	.1125232	.0000104
2,4-Dimethylhexane			5	5	2.52870 2.15555	.001975 .001956	.003063 .000986	.000430 .000365	.284691 .242613	.000415 .000392	.000032 .000018	.1124320	.0000049
2,5-Dimethylhexane			5	5	2.65585 2.08676	.001982 .001952	.002559 .000687	.000466 .000317	.298781 .235016	.000416 .000381	.000041 .000030	.1123625	.0000104
3,3-Dimethylhexane			5	5	2.77636 2.19862	.001976 .001957	.002761 .000901	.000430 .000302	.311844 .247923	.000415 .000392	.000034 .000020	.1124209	.0000036
3,4-Dimethylhexane			5	5	2.67840 2.52729	.001982 .001934	.002405 .000012	.000371 .000051	.301809 .284412	.000414 .000403	.000026 .000084	.1125389	.0000110
2-Methyl-3-ethylpentane		5		5	2.52729 2.92399	.001934 .001949	.000012 .001064	.000051 .000141	.284412 .328979	.000403 .000414	.000084 .000094	.1125857	.0000074

3-Methyl-3-ethylpentane.....			5	5	2.18795	.001968	.001965	.000354	.246577	.000403	.000027	.1125184	.0000067
					to	to	to	to	to	to			
					2.33820	.001971	.002452	.000429	.263508	.000419	.000033		
2,2,3-Trimethylpentane.....			5	5	2.16458	.001951	.000254	.000306	.243840	.000402	.000029	.1124337	.0000102
					to	to	to	to	to	to			
					2.90827	.001973	.002600	.000429	.327328	.000419	.000037		
2,2,4-Trimethylpentane.....	5	1	6	2.12289	.001920	.001037	.000061	.238699	.000405	.000022	.1123867	.0000086	
				to	to	to	to	to	to				
				2.58952	.001956	.002599	.000421	.290815	.000423	.000085			
2,3,3-Trimethylpentane.....			5	5	2.34094	.001943	.000989	.000330	.264472	.000409	.000030	.1125043	.0000091
					to	to	to	to	to	to			
					2.67128	.001963	.001971	.000362	.300999	.000426	.000034		
2,3,4-Trimethylpentane.....	5		5	2.45424	.001937	.001199	.000074	.276063	.000409	.000077	.1124729	.0000123	
				to	to	to	to	to	to				
				2.56721	.001950	.001516	.000102	.289019	.000422	.000084			

* The numbers in columns *A*, *B*, and *C* indicate the number of experiments performed with calorimeter systems *A*, *B*, and *C* (see section V-1 and section VII-1 of reference [4])

^b Samples I and II were used in the experiments with calorimeter systems *B* and *C*, respectively.

^c All the values of *B* were converted to apply to calorimetric system *C* (see section VII-1 of reference [4]).

TABLE 4.—Results of the calorimetric combustion experiments with gelatin

Experiment No. ^a	Mass of gelatin	Mass of benzoic acid	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_o	Δr_i	Δr_n	Δr (benzoic acid) ^b	<i>B'</i>	Deviation from mean	$\frac{\text{Mass CO}_2}{\text{Mass gelatin}}$	Deviation from mean
	<i>g</i>	<i>g</i>	<i>min</i> ⁻¹	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm/g gelatin</i>	<i>Ohm/g gelatin</i>	<i>g CO</i> ₂ / <i>g gelatin</i>	<i>g CO</i> ₂ / <i>g gelatin</i>
Series I:													
1	0.19019		0.001886	0.001343	0.000368	0.030331	0.000375	0.000098		0.156994	—0.000289	1.79184	—0.00047
2	.76263		.001923	.000530	.000317	.120500	.000384	.000410		.156977	—0.000306	1.78953	—0.00278
3	.72279		.001936	.000628	.000298	.114391	.000406	.000365		.157208	—0.000675	1.79145	—0.00086
4	.77277		.001927	.000532	.000304	.122587	.000418	.000400		.157588	—0.000305	1.79535	.00304
Series II:													
5	.19597	1.34079	.001957	.001171	.000395	.288651	.000415	.000180	0.257274	.156958	—0.000325	* 1.79339	.00108
6	.20141	1.34037	.001952	.001192	.000245	.289533	.000304	.000196	.257193	.157971	—0.000688		
Mean										0.157283		1.79231	
Standard deviation of the mean										±0.000169		±0.00098	

^a All of these experiments were performed with calorimeter system *C* (see section V-1 and section VII-1 of reference [4]).

^b Calculated from the mass of benzoic acid, using 26,428.4 int. J/g for the heat of the bomb process under standard conditions [11].

^c The mass of carbon dioxide arising from the benzoic acid was calculated from the mass of the benzoic acid, using a stoichiometrical value of unity, as determined in other experiments [12].

TABLE 5.—Results of the calorimetric combustion experiments on 2,2,3,3-Tetramethylbutane

Experiment No. ^a	Mass of gelatin	Total mass of carbon dioxide formed	Mass of carbon dioxide formed from 2, 2, 3, 3-tetramethylbutane	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_o	Δr_i	Δr_n	Δr (gelatin)	<i>B</i>	Deviation from mean
	<i>g</i>	<i>g</i>	<i>g</i>	<i>min</i> ⁻¹	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm/g CO</i> ₂	<i>Ohm/g CO</i> ₂
1	0.17509	3.91090	3.59708	0.001953	—0.002421	0.000211	0.431586	0.000407	0.000187	0.027539	0.1121590	—0.0000274
2	.18258	3.32958	3.00234	.001953	—0.00887	.000267	.366063	.000412	.000162	.028717	.1121662	—0.000202
3	.16505	2.24386	1.94804	.001939	.002432	.000307	.245180	.000415	.000177	.025960	.1122241	.0000377
4	.15359	2.59138	2.31610	.001944	.001387	.000277	.284606	.000427	.000152	.024157	.1121964	.0000100
Mean											0.1121864	
Standard deviation of the mean											±0.0000149	

^a All these experiments were performed with calorimeter system *C* (see section V-1 and section VII-1, of reference [4]).

TABLE 6.—Heats of isomerization of the octanes in the liquid (or solid) state ^a

Substance	State	<i>B</i> at 28.00° C	Ratio of the heats of combustion in the bomb process <i>B_i/B_n</i> at 28.00° C	Difference in the heats of combustion in the bomb pro- cess ^b $(-\Delta U_B)_n$ $-(-\Delta U_B)_i$; at 28° C	Heats of isomerization of the condensed phase <i>H_i</i> ° (liq or solid) $-H_n$ ° (liq) at 25° C	
				<i>Int. kj/mole</i>	<i>Int. kj/mole</i>	<i>kcal/mole</i>
<i>n</i> -Octane	Liquid	<i>Ohm/g CO₂</i> 0.1125810 ±0.0000124	1.000000	<i>Int. kj/mole</i> 0.00	<i>Int. kj/mole</i> 0.00	<i>kcal/mole</i> 0.00
2-Methylheptane	do	.1124730 ±0.0000142	0.999041 ±0.000168	5.23 ±0.92	-5.23 ±0.92	-1.25 ±0.22
3-Methylheptane	do	.1125282 ±0.0000100	.999531 ±0.000142	2.56 ±0.78	-2.56 ±0.78	-0.61 ±0.19
4-Methylheptane	do	.1125434 ±0.0000106	.999666 ±0.000145	1.82 ±0.79	-1.82 ±0.79	-.44 ±0.19
3-Ethylhexane	do	.1125690 ±0.0000078	.999893 ±0.000130	0.58 ±0.71	-0.58 ±0.71	-.14 ±0.17
2, 2-Dimethylhexane	do	.1123315 ±0.0000050	.997784 ±0.000119	12.10 ±0.65	-12.10 ±0.65	-2.89 ±0.16
2, 3-Dimethylhexane ^c	do	.1125232 ±0.0000208	.999487 ±0.000215	2.80 ±1.17	-2.80 ±1.17	-0.67 ±0.28
2, 4-Dimethylhexane	do	.1124320 ±0.0000098	.998677 ±0.000140	7.22 ±0.76	-7.22 ±0.76	-1.73 ±0.18
2, 5-Dimethylhexane	do	.1123625 ±0.0000208	.998059 ±0.000215	10.60 ±1.17	-10.60 ±1.17	-2.53 ±0.28
3, 3-Dimethylhexane	do	.1124209 ±0.0000072	.998578 ±0.000128	7.76 ±0.70	-7.76 ±0.70	-1.85 ±0.17
3, 4-Dimethylhexane	do	.1125389 ±0.0000220	.999626 ±0.000226	2.04 ±1.23	-2.04 ±1.23	-0.49 ±0.29
2-Methyl-3-ethylpentane	do	.1125857 ±0.0000148	1.000042 ±0.000172	-0.23 ±0.94	+0.23 ±0.94	+ .05 ±0.22
3-Methyl-3-ethylpentane	do	.1125184 ±0.0000134	0.999444 ±0.000162	3.04 ±0.88	-3.04 ±0.88	-.73 ±0.21
2, 2, 3-Trimethylpentane	do	.1124337 ±0.0000204	.998692 ±0.000212	7.14 ±1.16	-7.10 ±1.16	-1.70 ±0.28
2, 2, 4-Trimethylpentane	do	.1123867 ±0.0000172	.998274 ±0.000189	9.42 ±1.03	-9.38 ±1.03	-2.24 ±0.25
2, 3, 3-Trimethylpentane	do	.1125043 ±0.0000182	.999319 ±0.000196	3.72 ±1.07	-3.72 ±1.07	-0.89 ±0.26
2, 3, 4-Trimethylpentane	do	.1124729 ±0.0000246	.999040 ±0.000245	5.24 ±1.34	-5.25 ±1.34	-1.25 ±0.32
2, 2, 3, 3-Tetramethylbutane	Solid	.1121864 ±0.0000298	.996495 ±0.000287	19.13 ±1.57	-18.84 ±1.57	-4.50 ±0.38

^a All the uncertainties assigned to the experimental quantities in this table are equal to twice the standard deviation of the mean. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken, on the average, as ±0.25 kcal/mole, except that when one of the isomers is 2,2,3,3-tetramethylbutane the uncertainty may be taken as ±0.40 kcal/mole and except for 2,3-dimethylhexane, for which see footnote c below.

^b Obtained by subtracting the value in column 4 from unity and multiplying with the factor 5,458.8 int. kj/mole (see text).

^c The values assigned to 2,3-dimethylhexane may be uncertain by several times the amount indicated because of the uncertainty as to purity (see tables 1 and 2).

The values in column 6 differ from those in column 5 because of the difference in the heat capacities of the isomers over the range 25° to 28° C, the Washburn conversion to zero pressure [20], and the conversion of ΔU to $\Delta(U+PV)=\Delta H$. Account was taken of the effect of the gelatin and of benzoic acid on the Washburn correction of the results of the experiments given in tables 4 and 5.

In table 7 are given values for the following: The heat of isomerization, for the condensed phase, of *n*-octane into each isomer, at 25° C and 1 atm, as given in table 6; the difference, between *n*-octane and each isomer, in the heat of vaporization (sublimation for 2, 2, 3, 3-tetramethylbutane), at 25° C, as taken from the work of Osborne and Ginnings [5], reduced to the ideal state [10]; the heat of isomerization, for the ideal gaseous state, of *n*-octane into each isomer at 25° C; the difference, between *n*-octane and each isomer, in the value of $H_{298.16}^{\circ}-H_0^{\circ}$, the heat content at 298.16° K (25° C) referred to the absolute zero, for the ideal gaseous state [6]; and, finally, the energy of isomerization, for the ideal gaseous state, of *n*-octane into each isomer at 0° K.

TABLE 7.—Heats of isomerization of the octanes in the gaseous state ^a

Substance	Heat of isomerization of the condensed phase ^b $H_n^{\circ}(\text{liq or solid})-H_n^{\circ}(\text{liq})$ at 25° C		Difference in the heats of vaporization ^c $(\Delta H_v^{\circ})_n - (\Delta H_v^{\circ})_n$ at 25° C		Heat of isomerization of the gas $H_n^{\circ}(\text{g})-H_n^{\circ}(\text{g})$ at 25° C		$(H_{298.16}^{\circ}-H_0^{\circ})_n - (H_{298.16}^{\circ}-H_0^{\circ})_n$		Heat of isomerization of the gas $H_n^{\circ}(\text{g})-H_n^{\circ}(\text{g})$ at 0° K	
	int. kJ/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00	kcal/mole 0.00
<i>n</i> -Octane.....										
2-Methylheptane.....	-5.23±0.92	-1.25±0.22	.43±0.01	-1.68±0.22	-.59±0.20	-1.09±0.30				
3-Methylheptane.....	-2.56±0.78	-0.61±0.19	.39±0.01	-1.00±0.19	-.69±0.25	-0.31±0.31				
4-Methylheptane.....	-1.82±0.79	-.44±0.19	.43±0.01	-0.87±0.19	-.77±0.25	-.10±0.31				
3-Ethylhexane.....	-0.58±0.71	-.14±0.17	.44±0.01	-.58±0.17	-1.20±0.40	+ .62±0.43				
2, 2-Dimethylhexane.....	-12.10±0.65	-2.89±0.16	1.00±0.01	-3.89±0.16	-0.99±0.35	-2.90±0.39				
2, 3-Dimethylhexane ^d	-2.80±1.17	-0.67±0.28	0.64±0.01	-1.31±0.28	-.88±0.30	-0.43±0.41				
2, 4-Dimethylhexane.....	-7.22±0.76	-1.73±0.18	.89±0.01	-2.62±0.18	-1.21±0.40	-1.41±0.44				
2, 5-Dimethylhexane.....	-10.60±1.17	-2.53±0.28	.86±0.01	-3.39±0.28	-1.11±0.35	-2.28±0.45				
3, 3-Dimethylhexane.....	-7.76±0.70	-1.85±0.17	.94±0.01	-2.79±0.17	-1.22±0.40	-1.57±0.43				
3, 4-Dimethylhexane.....	-2.04±1.23	-0.49±0.29	.60±0.01	-1.09±0.29	-0.90±0.30	-0.19±0.42				
2-Methyl-3-ethylpentane.....	+0.23±0.94	+ .05±0.22	.71±0.01	-0.66±0.22	-1.03±0.35	+ .37±0.41				
3-Methyl-3-ethylpentane.....	-3.04±0.88	-.73±0.21	.81±0.01	-1.56±0.21	-1.21±0.40	-.35±0.45				
2, 2, 3-Trimethylpentane.....	-7.10±1.16	-1.70±0.28	1.09±0.01	-2.79±0.28	-1.35±0.45	-1.44±0.53				
2, 2, 4-Trimethylpentane.....	-9.38±1.03	-2.24±0.25	1.51±0.01	-3.75±0.25	-1.35±0.45	-2.40±0.52				
2, 3, 3-Trimethylpentane.....	-3.72±1.07	-0.89±0.26	1.02±0.01	-1.91±0.26	-1.23±0.40	-0.68±0.48				
2, 3, 4-Trimethylpentane.....	-5.25±1.34	-1.25±0.32	0.90±0.01	-2.15±0.32	-1.36±0.45	-.79±0.55				
2, 2, 3, 3-Tetramethylbutane.....	-18.84±1.87	-4.50±0.38	-.33±0.01	-4.17±0.38	-1.41±0.45	-2.76±0.59				

^a The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may be taken as ± 0.25 kcal/mole for the condensed phase at 25° C, ± 0.25 kcal/mole for the gas at 25° C, and ± 0.50 kcal/mole for the gas at 0° K, except for 2,2,3,3-tetramethylbutane for which the uncertainty is somewhat larger, and except for 2,3-dimethylhexane, for which see footnote "d" below.

^b All are liquid except 2, 2, 3, 3-tetramethylbutane, which is solid.

^c For the solid 2, 2, 3, 3-tetramethylbutane, the heat of sublimation is involved.

^d The values assigned to 2,3-dimethylhexane may be uncertain by several times the amount indicated because of the uncertainty as to purity (see tables 1 and 2).

VI. DATA OF PREVIOUS INVESTIGATIONS

The only published papers describing the determination of the heat of combustion of one or more octanes are the following:

Investigators	Year	Reference	Compounds
Zubow.....	1898	[14]	<i>n</i> -Octane
Richards and Jesse.....	1910	[15]	<i>n</i> -Octane 2-Methylheptane 3-Ethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane
Jessup.....	1928	[16]	<i>n</i> -Octane 2,2,4-Trimethylpentane 2,2,3,3-Tetramethylbutane
Banse and Parks.....	1933	[17]	<i>n</i> -Octane
Jessup.....	1937	[18]	<i>n</i> -Octane

Of the foregoing data, only those of Richards and Jesse [15] and of Jessup [16] yield values for the heats of isomerization of any of the octanes.

The data of Richards and Jesse [15] yield the following values for the ratio of the heat of combustion of a given isomer to the heat of combustion of *n*-octane: *n*-octane, 1.0000; 2-methylheptane, 1.0010; 3-ethylhexane, 0.9983; 2,5-dimethylhexane, 0.9990; 3,4-dimethylhexane, 0.9993. The corresponding values of heats of isomerization for the four isoparaffins become, for *n*-octane into a given isomer, in the liquid state, $\Delta H = +1.3, -2.2, -1.3, -0.9$ kcal/mole, respectively. The corresponding values from the present investigation are $-1.25, -0.14, -2.53, -0.49$ kcal/mole, respectively. Since the values from Richards and Jesse may be uncertain by as much as 2 kcal/mole or more, it is seen that their data are substantially in accord with those of the present investigation within the respective limits of uncertainty.

The data of Jessup [16] were obtained in an investigation in which circumstances made it possible to perform only two complete combustion experiments on each of three isomers. His data yield, for the heat of isomerization of liquid *n*-octane into liquid 2,2,4-trimethylpentane and into solid 2,2,3,3-tetramethylbutane, $\Delta H = -1.8$ and -3.2 kcal/mole, respectively. The corresponding values from the present investigation are -2.24 and -4.50 kcal/mole. Because of the then unavoidable limitations placed upon these experiments of Jessup, the values of heats of isomerization deduced from them are arbitrarily assigned an uncertainty of ± 1.0 kcal/mole. It is seen that Jessup's values are in accord with those of the present investigation within the respective limits of uncertainty.

VII. DISCUSSION

As has been previously pointed out, values of the heats of isomerization of the octanes, along with those of the other paraffin hydrocarbons, are needed in calculating, in combination with free-energy functions, values of the free energies of isomerization and in studying

the influence of structure upon the energy content of the molecule.

With regard to the correlation of the energy content with structure, a separate report will be made. It may be pointed out here, however, that the data on the energies of isomerization of the octanes are in accord with the generalization previously made [1, 3] concerning the change with structure of the energy content of hydrocarbons.

The use of these data on energies of isomerization for calculating equilibria and free energies of isomerization of the 18 octanes is discussed in another report [13].

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