HEATS OF FORMATION OF GASEOUS HYDROCARBONS[1]

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The existing data leading to values of the heats of formation of hydrocarbons in the gaseous state are discussed. "Best" values are given for the heats of formation of eight paraffin hydrocarbons (through the pentanes), sixteen olefin hydrocarbons (through the pentenes), and three acetylene hydrocarbons, all in the gaseous state. Regularities and irregularities in the heats of formation, and their changes with structure, are discussed. Forthcoming data on the hexanes are mentioned.

I. INTRODUCTION

In a review entitled "Heats of Formation of Simple Organic Molecules" (32), published in 1937, it was pointed out that until about ten years ago the great body of the thermochemical data on organic compounds was dependent upon experimental results obtained in the European laboratories of Thomsen, Berthelot, Louguinine, Zubow, Stohmann, and others, in the period from about 1860 to 1900, together with some data obtained in the United States by Richards and his coworkers from about 1905 to 1915. It was stated also (32) that (*a*) the "early investigators and their coworkers performed exceedingly well with the more or less impure materials available to them", (*b*) the "old data fall short of meeting the present-day requirements of accuracy, which have increased ten-fold or more in the past half-century", and (*c*) "practically none of the old data on organic compounds can be used in thermodynamic calculations where errors in ΔH of several kilocalories per mole are significant."

In the old days, a kilocalorie of energy was often considered quite negligible. Today, however, such an amount of energy may determine the success or failure of a proposed chemical process for making a desired substance of commerce. A difference of energy of 3.1 kcal. per mole is sufficient to change the equilibrium constant of a given reaction at room temperature by a factor of 200. For example, in an equilibrium at room

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temperature between the two gaseous substances A and B, calculated to be present at equilibrium in amounts of 10 and 90 per cent, respectively, a reduction of 3.1 kcal. per mole in the energy content of A would change the calculated equilibrium concentration of A from 10 per cent to over 95 per cent.

Present-day requirements for values of heats of formation place a heavy burden upon accuracy and precision in thermochemical measurements. Any given thermochemical investigation involves fundamentally, either directly or indirectly, the performance of two kinds of experiments. In one of these there is measured the amount of chemical reaction whose occurrence produces a specified change in the calorimeter, and in the other the quantity of electrical energy that produces the same change in the calorimeter (31). The chemical procedure and the calorimetric procedure are equally important in establishing the accuracy of the final thermochemical value.

The need for high accuracy is illustrated in the determination of the difference in the energy contents of the five isomers of hexane, which differences are of the order of 1 to 5 kcal. per mole. Since there is no simple chemical process susceptible of calorimetric measurement that involves the transformation of the various isomers, one into the other, one must select for measurement a series of five chemical reactions in which all the reactants and products are the same except the given isomer of hexane. When calorimetric observations are made on these chemical reactions under conditions which are substantially identical, the differences in the observed thermochemical values will be the differences in the heat or energy contents of the corresponding isomers of hexane. There is at present only one type of chemical reaction that can be used in this manner to determine the differences in the energy contents of the various isomers of hexane, and that is the reaction of combustion of the hydrocarbon in oxygen. Now the heat of combustion of normal hexane is about 1000 kcal. per mole, and the heats of combustion of the other isomers will differ from the value for normal hexane by only about 1 to 5 kcal. per mole. The determination of the difference in the energy contents of the various hexanes, therefore, depends significantly upon the chemical and calorimetric precision with which the heat of combustion of a given mass of the hydrocarbon can be determined. If the heat of combustion of each hexane can be determined with an estimated uncertainty of 1 part in 1000, or ±1.0 kcal. per mole, then the difference in the values for any two of the hexanes will have an estimated uncertainty of ±1.4 kcal. per mole (34). This uncertainty is too large to determine satisfactorily quantities of the order of 1 to 5 kcal. per mole. However, if the measurement of the heat of combustion can be made with an estimated uncertainty of only 2 parts in 10,000, then the difference in the energy contents of any two of the isomers can be determined with an estimated uncertainty of only ±0.3 kcal. per mole. This is substantially the limit of the accuracy obtainable with present-day thermochemical apparatus and technic (31).

There are a number of cases where the difference in the heats of formation of two hydrocarbons can be determined from calorimetric measurements of a simple chemical reaction in which one of the hydrocarbons is a reactant, the other is a product, and any other reactants or products are elemental substances. Examples of this procedure and type of reaction include the determination, by measurement of the heat of hydrogenation, of the difference in the heats of formation of (*a*) a monoölefin or diolefin hydrocarbon and the corresponding paraffin, (*b*) an aromatic or partially hydrogenated aromatic hydrocarbon and the corresponding naphthene (cycloparaffin) hydrocarbon, and (*c*) an acetylene hydrocarbon and the corresponding paraffin hydrocarbon.

When the hydrogenated product is the same for two different unsaturated hydrocarbons, either olefinic or aromatic, the difference in the heats of hydrogenation will give the difference in the heats of formation of the corresponding unsaturated hydrocarbons. In this way, one can determine the differences in the heats of formation of all those unsaturated hydrocarbons having the same number and skeletal arrangement of carbon atoms in the molecule, provided the reaction of hydrogenation is clear-cut and susceptible of calorimetric measurement.

In the determination of heats of combustion, the estimated uncertainty, in calories per mole, is roughly proportional to the number of carbon atoms per molecule of the given substance, whereas, in heats of hydrogenation, the estimated uncertainty is (all other things being equal) substantially proportional to the number of moles of hydrogen added to 1 mole of the unsaturated hydrocarbon. In actual values of energy, and in percentages of the total amount of energy measured per mole of the substance investigated, estimated uncertainties have been reported as given in table 1 for determinations of heats of combustion and heats of hydrogenation. For the representative examples given, which, for the heats of combustion, are taken from the work of Rossini and collaborators at the National Bureau of Standards and, for the heats of hydrogenation, from the work of Kistiakowsky and collaborators at Harvard University, the average estimated over-all uncertainty is $\pm 0.02_4$ per cent for the combustion experiments and ±0.20 per cent for the hydrogenation experiments. It is obvious that, notwithstanding the lower percentage uncertainty attainable in the combustion experiments, the hydrogenation experiments possess a decided advantage in the actual uncertainty in kilocalories per mole as one goes to the larger molecules. The hydrogenation method is therefore to be preferred, wherever possible, in determining the difference in the heats of formation of a given unsaturated hydrocarbon and the corresponding saturated hydrocarbon, as 1-butene and *n*-butane, in determining the difference in the energy contents of two unsaturated isomeric hydrocarbons yielding the same hydrocarbon on hydrogenation, as 1-butene and 2-butene, and in determining the difference in the heats of formation of any two unsaturated hydrocarbons yielding the same hydrocarbon on hydrogenation, as 1-butene and 1,3-butadiene. The difference in the energy contents or heats of formation of two unsaturated hydrocarbons that do not yield the same paraffin hydrocarbon on hydrogenation can not be determined from hydrogenation experiments alone, and recourse must be had to combustion experiments alone or to a combination of combustion experiments and hydrogenation experiments. For example, suppose it is desired to know the difference in the energy contents (or heats of formation) of 1-butene and "isobutene" (2-methylpropene). This quantity can be evaluated in two different ways: (*a*) as the difference in the heats of combustion of 1-butene and "isobutene"; or (*b*) as the sum of the difference in the heats of hydrogenation of 1-butene and "isobutene" with the corresponding difference in the heats of combustion of *n*-butane and isobutane. Both methods should, of course, yield the same value within their respective limits of uncertainty.

TABLE 1

Estimated uncertainties for determinations of heats of combustion and heats of hydrogenation

SUBSTANCE	ESTIMATED OVER-ALL UNCERTAINTY FROM COMBUSTION EXPERIMENTS		ESTIMATED OVER-ALL UNCERTAINTY FROM HYDROGENATION EXPERIMENTS	
	kcal. per mole	*percentage*	*kcal. per mole*	*percentage*
C_2H_4	± 0.07	$\pm 0.02_1$	± 0.06	± 0.18
C_2H_6	± 0.11	$\pm 0.02_8$		
C_3H_6	± 0.15	$\pm 0.03_0$	± 0.06	± 0.20
C_3H_8	± 0.12	$\pm 0.02_3$		
C_4H_8			± 0.06	± 0.20
C_4H_{10}	± 0.14	$\pm 0.02_0$		
C_5H_{12}	± 0.20	$\pm 0.02_4$		
C_7H_{14}			± 0.06	± 0.20

II. UNITS OF ENERGY

The actual unit of energy in calorimetric investigations today is the international joule, which is derived from the mean solar second and the international electrical watt. The international electrical watt is based upon standards of electromotive force and resistance maintained in terms of international volts and international ohms at the various national standardizing laboratories. Conversion to the artificial calorie may be made by means of the definition

$$1 \text{ calorie} = 4.1833 \text{ international joules}$$

The International Committee on Weights and Measures, through its Advisory Committee on Electricity, had planned that the various national standardizing laboratories in 1940 would begin to calibrate standard cells and resistances in terms of absolute instead of international units (1), but conditions abroad have made necessary a postponement of the plan. However, when international agreement is obtained on the best relation between the international and absolute electrical units, it is expected that the national standardizing laboratories will calibrate standard cells and resistances in terms of absolute volts and absolute ohms. At that time, the actual unit of energy in calorimetric measurements will become the absolute watt (electrical), which will be as nearly equal to 10^7 ergs per second as present-day measurements will permit. In order then to retain the same artificial calorie as is at present being used in thermochemical reports and writings, a new factor for conversion to the artificial calorie may be used. The definition of the artificial calorie will then become

$$1 \text{ calorie} = (4.1833)(1 + a) \text{ absolute joules}$$

where $(1 + a)$ will be the then best value for the number of absolute watts in 1 international watt. At the present time, the best relation between the international watt and the absolute watt appears to be that derived from measurements of the absolute ohm and absolute ampere recently made at the National Bureau of Standards at Washington (5, 6, 7, 42) and at the National Physical Laboratory at London (12, 40, 41). These determinations are in excellent accord with one another and yield the relation

$$1 \text{ international watt} = 1.00020 \pm 0.00005 \text{ absolute watts}$$

The results of preliminary measurements made of the relation between the international ampere and the absolute ampere at the Physikalisch-Technische Reichsanstalt at Berlin (1) lead to a value several parts in 10,000 greater than that given above. It is hoped that this difference will be resolved at an early date.

III. STANDARD REFERENCE STATES

Following the practice of Lewis and Randall (21), the standard reference temperature is taken as 25°C., and the standard reference states for individual substances are taken as follows: For a liquid or solid substance, the standard reference state is the actual pure liquid or solid at a pressure of 1 atm. at the given temperature; for a gaseous substance, the standard reference state is the gas in the hypothetical state of unit fugacity (1 atm.), where the heat content is the same as that of the real gas at zero pressure. In each case, the standard state is indicated by a superscript zero attached to the letter symbol indicating the thermodynamic property involved, here the heat content, H^0.

In the case of a solid substance that exists in two crystalline forms, it is necessary to specify that form that is to serve as the standard reference state for the given substance. In the case of carbon, some uncertainty formerly existed with regard to the possible forms of graphite, and, in one compilation (3), diamond was selected as the standard reference state for carbon. However, a recent investigation on the thermochemistry of carbon, carried on coöperatively by the National Bureau of Standards and the Coal Research Laboratory of the Carnegie Institute of Technology, has shown that the existence of more than one form of graphite is extremely improbable, and there is now every reason to use graphite as the standard reference state for carbon (8, 14, 35).

When values of the heats of formation at 25°C. are to be converted to the corresponding ones at 0°K., for use in connection with statistically calculated values of the free-energy function, $(F^0 - H^0_0)/T$, the following values may be used for $H^0_{298.16} - H^0_0$, the heat content at 25°C. referred to 0°K., for graphite and hydrogen: C(c, graphite), 1053.8 ± 12.5 int. j. per mole or 251.9 ± 3.0 cal. per mole; H_2(g), 8466.6 ± 2.0 int. j. per mole or 2023.9 ± 0.5 cal. per mole (33).

IV. HEATS OF FORMATION OF WATER AND CARBON DIOXIDE

In calculating the heats of formation of hydrocarbons from carbon and hydrogen in their standard states, the values of the heats of combustion of the hydrocarbons are combined with values for the heats of formation of water and carbon dioxide from their elements in the standard states. In the case of the unsaturated hydrocarbons whose heats of hydrogenation have been measured, the heat of formation of the unsaturated hydrocarbon may be calculated by combining the heat of hydrogenation with the heat of formation of the paraffin hydrocarbon, determined as just mentioned.

In order that all such tabulations of heats of formation shall be self-consistent and the values comparable with one another, it is important that selected "standard" values for the heats of formation of water and carbon dioxide be used throughout. While actually not necessary except for calculating heats of reaction in which solid carbon or gaseous hydrogen, or both, are among the reactants or products, it is desirable that the "standard" values used for the heats of formation of water and carbon dioxide be ones measured with an accuracy at least as great as that of any other thermochemical quantity of similar magnitude. Reliable values of heats of formation are now available for both water and carbon dioxide.

For the heat of formation of water from gaseous hydrogen and oxygen at 25°C., the following value has been reported[2] (33):

$$H_2(g) + \frac{1}{2} O_2(g) = H_2O(liq); \Delta H^0_{298.16} = -285{,}795 \pm 40 \text{ int. j. per mole} = -68{,}318.1 \pm 9.6 \text{ cal. per mole}$$

For the heat of formation of carbon dioxide from solid carbon (graphite) and gaseous oxygen at 25°C., the following value has been reported (33, 35):

$$C(c, \text{graphite}) + O_2(g) = CO_2(g); \Delta H^0_{298.16} = -393{,}355 \pm 46 \text{ int. j. per mole} = -94{,}029.8 \pm 11.0 \text{ cal. per mole}$$

(The above values expressed in calories are carried to more figures than are significant, so that one may recover the original value expressed in international joules on reconversion to that unit by means of the factor 4.1833.)

V. EXISTING DATA ON GASEOUS HYDROCARBONS

For the gaseous hydrocarbons, the existing thermochemical data that have been obtained with modern calorimetric apparatus and technic, and with due regard for the accuracy of the chemical as well as the calorimetric procedure, are, with the exception of data on one compound, all from the thermochemical laboratories at Harvard University and the National Bureau of Standards. The data from the latter laboratory are all on heats of combustion and those from the former are all on heats of hydrogenation.

The present review is limited to those hydrocarbons containing eight or less carbon atoms per molecule, and to those determinations made within the past fifteen years. The previous review (32) includes references to all the earlier work on these compounds. References to data on hydrocarbons in the liquid state are also included here, since these may be converted to the gaseous state by combination with the appropriate heats of vaporization. Unfortunately, however, no heats of vaporization of hydrocarbons above pentane have heretofore been measured at or near 25°C., and values calculated for this temperature, either from calorimetric data at the normal boiling point or from existing data on the vapor pressure-temperature relations, introduce an additional uncertainty into the values so derived for the heats of formation in the gaseous state.

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[2] The following symbols are used to designate the physical state of a substance: c = crystal; liq = liquid; g = gas.

For paraffin hydrocarbons in the gaseous state, measurements of the heat of combustion were made on the following: methane (26), ethane (27), propane (27), *n*-butane (27), isobutane (30), *n*-pentane (27), 2-methylbutane (19, 39), and tetramethylmethane (19). For paraffin hydrocarbons in the liquid state, measurements of the heat of combustion were made on the following: *n*-hexane (13), *n*-heptane (13), and *n*-octane (13, 2).

For olefin hydrocarbons in the gaseous state, measurements of the heat of combustion were made on ethylene (36) and propylene (36), and measurements of the heat of hydrogenation were made on the following: ethylene (15), propylene (16), 1-butene (16), *trans*-2-butene (16), *cis*-2-butene (16), "isobutene" (16), 1-heptene (17), 2-pentene (mixture of *cis* and *trans*) (17), 2-methyl-1-butene (17), 2-methyl-2-butene (17), 3-methyl-1-butene (9), 2,3-dimethyl-1-butene (17), 2,3-dimethyl-2-butene (17), 3,3-dimethyl-1-butene (9), 4,4-dimethyl-1-pentene (9), 2,4,4-trimethyl-2-pentene (9), 2,4,4-trimethyl-1-pentene (9), allene (18), 1,3-butadiene (18), 1,3-pentadiene (9), 1,4-pentadiene (18), 1,5-hexadiene (18), and 2,3-dimethyl-1,3-butadiene (30).

For unsaturated cyclic (including aromatic) hydrocarbons in the gaseous state, measurements of the heat of hydrogenation were made on the following: cyclopentene (9), cyclopentadiene (18), cyclohexene (17), 1,3-cyclohexadiene (18), cycloheptene (4), cycloheptadiene (4), cycloheptatriene (4), cyclooöctene (4), benzene (18), *o*-xylene (9), ethylbenzene (9), and vinylbenzene (9).

For acetylene hydrocarbons in the gaseous state, data on the heat of hydrogenation were reported for acetylene (4), methylacetylene (4), and dimethylacetylene (4).

For naphthene or cycloparaffin hydrocarbons in the gaseous state, modern data on the heat of combustion have so far been obtained only for cyclopropane (20). For naphthene hydrocarbons in the liquid state, data on the heat of combustion have been reported for methylcyclopentane (22) and cyclohexane (22).

VI. TABULATED VALUES OF HEATS OF FORMATION

In table 2 are given values for the heats of formation, from solid carbon (graphite) and gaseous hydrogen, of a number of paraffin, olefin, and acetylene hydrocarbons in the gaseous state at 25°C. These values were calculated by combining the "standard" values of the heats of formation of water and carbon dioxide with the appropriate data on the heats of combustion and hydrogenation of the hydrocarbons in the gaseous state. The values for the eight paraffin hydrocarbons listed are dependent upon the data on heats of combustion. The values for ethylene and propylene are weighted means of values derived from the data on heats of combustion alone and from a combination of data on heats of hydrogenation and the values for the heats of formation of the corresponding paraffins. The values for all the other olefins and for the acetylenes are derived from a combination of the data on heats of hydrogenation with the values for the heats of formation of the corresponding paraffins.

TABLE 2

Heats of formation of gaseous hydrocarbons from solid carbon (graphite) and gaseous hydrogen at 25°C.

SUBSTANCE	FORMULA AND STATE	$\Delta Hf^\circ_{298.16}$	
		int. j. per mole	*cal. per mole**
Paraffins:			
Methane	$CH_4(g)$	−74,735 ± 310	−17,865 ± 74
Ethane	$C_2H_6(g)$	−84,465 ± 450	−20,191 ± 108
Propane	$C_3H_8(g)$	−103,535 ± 520	−24,750 ± 124
n-Butane	$C_4H_{10}(g)$	−124,305 ± 640	−29,715 ± 153
Isobutane	$C_4H_{10}(g)$	−131,145 ± 550	−31,350 ± 132
n-Pentane	$C_5H_{12}(g)$	−145,325 ± 890	−34,739 ± 213
2-Methylbutane	$C_5H_{12}(g)$	−153,405 ± 640	−36,671 ± 153
Tetramethylmethane	$C_5H_{12}(g)$	−164,865 ± 950	−39,410 ± 227
Monoölefins:			
Ethylene	$C_2H_4(g)$	52,526 ± 280	12,556 ± 67
Propylene	$C_3H_6(g)$	20,732 ± 460	4,956 ± 110
1-Butene	$C_4H_8(g)$	1,602 ± 750	383 ± 180
cis-2-Butene	$C_4H_8(g)$	−5,806 ± 750	−1,388 ± 180
trans-2-Butene	$C_4H_8(g)$	−9,781 ± 750	−2,338 ± 180
"Isobutene" (2-methylpropene)	$C_4H_8(g)$	−13,407 ± 690	−3,205 ± 165
1-Pentene	$C_5H_{10}(g)$	−19,427 ± 1260	−4,644 ± 300
cis-2-Pentene	$C_5H_{10}(g)$	−26,794 ± 1260	−6,405 ± 300
trans-2-Pentene	$C_5H_{10}(g)$	−30,756 ± 1260	−7,352 ± 300
2-Methyl-1-butene	$C_5H_{10}(g)$	−35,240 ± 840	−8,424 ± 200
3-Methyl-1-butene	$C_5H_{10}(g)$	−27,518 ± 750	−6,578 ± 180
2-Methyl-2-butene	$C_5H_{10}(g)$	−41,812 ± 750	−9,995 ± 180
Diolefins:			
Allene	$C_3H_4(g)$	192,624 ± 1090	46,046 ± 260
1,3-Butadiene	$C_4H_6(g)$	112,384 ± 1000	26,865 ± 240
1,3-Pentadiene	$C_5H_8(g)$	79,002 ± 1260	18,885 ± 300
1,4-Pentadiene	$C_5H_8(g)$	106,946 ± 1260	25,565 ± 300
Acetylenes:			
Acetylene	$C_2H_2(g)$	226,852 ± 980	54,228 ± 235
Methylacetylene	$C_3H_4(g)$	185,358 ± 1000	44,309 ± 240
Dimethylacetylne	$C_4H_6(g)$	147,340 ± 1490	35,221 ± 355

* See the text for a discussion of the unit of energy.

VII. DISCUSSION

The hydrocarbons for which values of heats of formation are given in table 2 include only those on which calorimetric measurements were made on the hydrocarbon in the gaseous state. Values for those hydrocarbons whose heats of combustion in the liquid state only have been measured are withheld until reliable values for their heats of vaporization at 25°C. become available.

The values listed in table 2 for the heats of formation of the gaseous paraffin hydrocarbons indicate, within the limits of uncertainty with which measurements can be made today, that (*a*) the energy increment per CH_2 group is not constant for the gaseous normal paraffins from methane to pentane, and (*b*) the energy content of isomers is not constant, being less for the branched-chain isomers than for the straight-chain ones, and, for the pentanes, least for the most highly branched isomer, tetramethylmethane (neopentane). The fact that the differences between *n*-butane and isobutane (1.64 ± 0.20 kcal. per mole) and between *n*-pentane and 2-methylbutane (1.93 ± 0.26 kcal. per mole) are identical within their respective limits of uncertainty might lead one to expect a similar decrease in the energy content of a paraffin hydrocarbon for each single branch anywhere along its chain of carbon atoms. Likewise, one might expect that a double or neopentyl branching on one carbon atom anywhere in the molecule would produce a decrease in energy content substantially identical with that observed for the isomerization of *n*-pentane into tetramethylmethane (4.67 ± 0.31 kcal. per mole). It was with the thought of checking these expectations that a thermochemical investigation of the five hexanes was undertaken at the National Bureau of Standards (38). While this investigation has not yet been completed, the preliminary calculations indicate that, within the limits of uncertainty with which the measurements have been made, the assumptions relating to the constancy of the decrease in energy content for all single branches and for all double branches on the same carbon atom are not true. It appears that data on certain hydrocarbons above the hexanes will be necessary before estimates, having limits of uncertainty comparable to those attached to the experimental values, can be made for all the paraffin hydrocarbons in the gaseous state.

The thermochemical data now being obtained at the National Bureau of Standards on the hexanes and several higher paraffin hydrocarbons (38) will make possible (*a*) the evaluation of the heats of formation of these hexanes and higher hydrocarbons, (*b*) the evaluation of the heats of formation of the corresponding olefins whose heats of hydrogenation have already been measured (4, 9, 17, 18), (*c*) an improvement in the accuracy of the extrapolation of the heats of formation of the gaseous normal paraffins beyond pentane and hexane (see reference 28), (*d*) a similar improvement in the accuracy of the extrapolation of the heats of formation of the gaseous normal olefins (1-alkenes) (see reference 37), (*e*) a reliable estimation of the heats of formation of all the remaining branched-chain paraffin hydrocarbons in the gaseous state that will not have been measured, and (*f*) a similar reliable estimation of the heats of formation of the remaining gaseous olefin hydrocarbons that will not have been measured.

In considering differences in the energy contents of isomeric hydrocarbons, and, in general, changes in the energy content corresponding to structural changes in hydrocarbons, it is desirable when possible to compare the appropriate values of the heats of formation for 0°K. rather than for 25°C., in order to eliminate the translational, rotational, and ordinary vibrational energy. For this purpose, there are required values of $H^0_{298.16} - H^0_0$, the heat content at 25°C. referred to 0°K., for solid carbon (graphite), gaseous hydrogen, and the gaseous hydrocarbons. Values for carbon and hydrogen have already been given (see page 6). Values for a number of the gaseous hydrocarbons have already been calculated (24) and others are being calculated (25). For the butanes and pentanes, the effect of the elimination of the rotational and ordinary vibrational energy is to reduce significantly the magnitude of the difference in the energy contents of two given isomers, as follows:

ISOMERIZATION	$\Delta H^0_{298.16}$	$\Delta H^0_{298.16} - \Delta H^0_0$	ΔH^0_0
	kcal. per mole	*kcal. per mole*	*kcal. per mole*
(*n*-butane) = (isobutane)	-1.64 ± 0.20	-0.37 ± 0.07	-1.27 ± 0.21
(*n*-pentane) = (2-methylbutane)	-1.93 ± 0.26	-0.51 ± 0.07	-1.42 ± 0.27
(*n*-pentane) = (tetramethylmethane)	-4.67 ± 0.31	-0.63 ± 0.07	-4.04 ± 0.32

In table 3 are given values for the relative energy contents, at 0°K., of the isomers of butane and those of pentane, referred respectively to *n*-butane and *n*-pentane as zero. These values were derived from heats of combustion, with the corrections to 0°K. being made with the values of $H^0_{298.16} - H^0_0$ provided by Pitzer (25). At 0°K., then, where the molecules possess no translational, no rotational, and no ordinary vibrational energy, isobutane is more stable than *n*-butane by 1.27 ± 0.21 kcal. per mole. Likewise, 2-methylbutane is more stable than *n*-pentane by 1.42 ± 0.27 kcal. per mole, and tetramethylmethane is more stable than *n*-pentane by 4.04 ± 0.32 kcal. per mole.

Table 4 gives similar information for the butenes, with the values for *cis*-2-butene and *trans*-2-butene being derived from heats of hydrogenation and that for "isobutene" from a combination of heats of hydrogenation with heats of combustion. The corrections to 0°K. were made with values of $H^0_{298.16} - H^0_0$ provided by Pitzer (25). At 0°K., *cis*-2-butene is more stable than 1-butene by 1.84 ± 0.12 kcal. per mole, *trans*-2-butene by 2.79 ± 0.12 kcal. per mole, and "isobutene" by 3.85 ± 0.25 kcal. per mole.

TABLE 3

Energies of isomerization of the butanes and of the pentanes

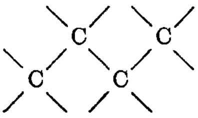
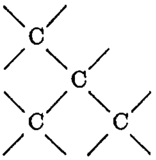
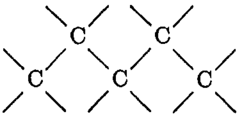
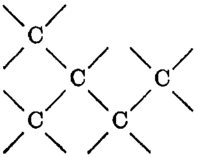
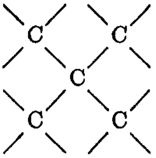
COMPOUND	STRUCTURE	RELATIVE ENERGY CONTENT AT 0°K. *kcal. per mole*
n-Butane		0.00
Isobutane		−1.27 ± 0.21
n-Pentane		0.00
2-Methylbutane		−1.42 ± 0.27
Tetramethylmethane		−4.04 ± 0.32

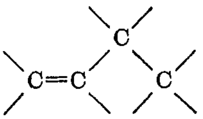
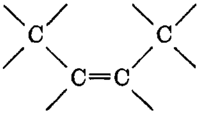
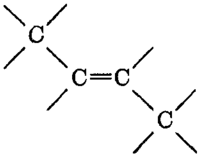
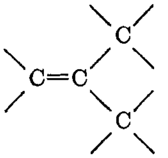
Table 5 gives similar information for four of the six pentenes (the values for *cis*-2-pentene and *trans*-2-pentene not being included because they were not measured separately). These values were derived from a combination of heats of hydrogenation and heats of combustion. At

25°C., with regard to energy content, 3-methyl-1-butene is more stable than 1-pentene by 1.93 ± 0.30 kcal. per mole, 2-methyl-1-butene by 3.78 ± 0.30 kcal. per mole, and 2-methyl-2-butene by 5.35 ± 0.30 kcal. per mole.

The energy of isomerization of 1,4-pentadiene into 1,3-pentadiene, as derived from heats of hydrogenation (see table 2), is $\Delta H^0_{298.16} = -6.68 \pm 0.25$ kcal. per mole. With regard to energy content, the 1,3-pentadiene is thus more stable by nearly 7 kcal. per mole.

TABLE 4

Energies of isomerization of the butenes

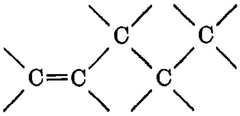
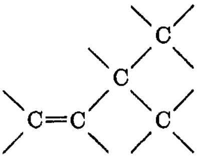
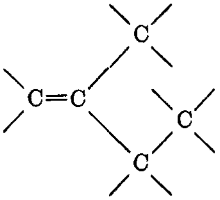
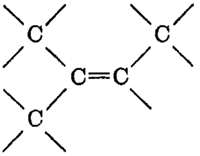
COMPOUND	STRUCTURE	RELATIVE ENERGY CONTENT AT 0°K.
		kcal. per mole
1-Butene		0.00
cis-2-Butene		−1.84 ± 0.12
trans-2-Butene		−2.79 ± 0.12
"Isobutene" (2-methylpropene)		−3.85 ± 0.25

While sufficient data are not yet available to make reliable quantitative estimates of the specific effects, the differences in the energy contents of isomers and the lack of constancy of the energy increment per CH_2 group may be ascribed to interactions between near neighbor atoms not directly bonded to one another. This interaction between non-bonded neighboring atoms was deduced from the data on the heats of combustion of paraffin hydrocarbons and normal alkyl primary alcohols (28, 29) and definitely confirmed by the data on heats of hydrogenation of olefin hydrocarbons, a complete discussion of which has recently appeared (4). Theoretical evaluations of the magnitude of such interactions have not yet been successfully made (10, 11).

Similar effects of interaction between non-bonded near-neighbor atoms have been found among the unsaturated cyclic hydrocarbons (4), although additional data are required before a complete interpretation can be made. This need for additional data is also true for the hydrocarbons of the aromatic and naphthene series. The aromatic ring nuclei involve consideration also of the "resonance" energy (23), and the naphthene ring nuclei of the departure of the bond angles from the normal tetrahedral value.

TABLE 5

Energies of isomerization of the pentenes

COMPOUND	STRUCTURE	RELATIVE ENERGY CONTENT AT 25°C.
		kcal. per mole
1-Pentene		0.00
3-Methyl-1-butene		−1.93 ± 0.30
2-Methyl-1-butene		−3.78 ± 0.30
2-Methyl-2-butene		−5.35 ± 0.30

On the basis of the data which are now available, it appears that the following factors impart greater stability to hydrocarbon molecules: (*a*) resonance, (*b*) minimum departure of the bond angles from the tetrahedral value, (*c*) maximum compactness of the carbon skeleton, and (*d*) minimum of repulsion between non-bonded atoms.

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