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HEAT OF HYDROGENATION OF ETHYLENE

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ABSTRACT

Extremely discordant values have been reported in recent years for the scientifically and industrially important thermodynamic quantity, the heat of hydrogenation of ethylene to ethane. From the value for the heat of combustion of ethylene recently obtained at the National Bureau of Standards by Rossini and Knowlton, and the values previously obtained by Rossini for the heats of combustion of hydrogen and ethane, a new value is deduced for the heat of hydrogenation of ethylene. The four earlier sets of calorimetric data leading to this quantity have been reviewed, and the following values deduced for $-\Delta H^\circ$ at 25° C for the reaction, $C_2H_4\ (g) + H_2\ (g) = C_2H_6\ (g)$, in kilocalories per mole: Thomsen (1873–86), 32.3 ±1.5; Berthelot and Matignon (1893), 37.6 ±1.9; Von Wartenberg and Krause (1930), 30.6 ±0.4; Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan (1935), (*a*) 32.58 ±0.06, (*b*) 32.64 ±0.06; National Bureau of Standards (1931–36), 32.78 ±0.13. (In deducing the estimated uncertainties, no allowance has been made for possible "unknown" systematic errors). It is concluded that the true heat of hydrogenation at 25° C lies in the immediate neighborhood of the last two values. The value of $-\Delta H^\circ$ obtained by Teller and Topley and others, by combination of entropies computed statistically with the free energy determined experimentally, is apparently low by from 1.6 to 1.7 kilocalories per mole. The explanations of this discrepancy are briefly reviewed.

CONTENTS

I. INTRODUCTION

The heat of hydrogenation of ethylene to form ethane has become, in recent years, a thermal quantity of considerable interest and speculation, the latter arising from the extreme discord among the existing values for this property, for which two modern values differ by 7 percent. In addition to the practical importance of this quantity in thermodynamic calculations, it possesses importance in connection with the proper description of the molecules for the purpose of computing, by statistical methods, values of their entropies and heat contents as functions of the temperature. In the case of ethane, for example, this latter consideration includes the question of how much restriction, if any, exists in the rotation of the methyl groups about the carbon-carbon linkage.

Because of the recent completion by Rossini and Knowlton [1] [1] [2] of measurements on the heat of combustion of ethylene, the data on which can be combined with data previously reported by Rossini [2] on the heats of combustion of hydrogen and ethane to obtain a value for the heat of hydrogenation of ethylene, it seems desirable to review the data which may be utilized to obtain values for the heat of the reaction

$$C_2H_4\ (g)+H_2\ (g)=C_2H_6\ (g) \qquad (1)$$

There are two ways in which the heat of the above reaction may be determined from calorimetric data: first, from data on the direct reaction of hydrogenation according to equation 1; and, second, from data on the heats of combustion of ethylene, hydrogen, and ethane:

$$C_2H_4\ (g)+3\ O_2\ (g)=2\ CO_2\ (g)+2\ H_2O\ (liq) \qquad (2)$$

$$H_2\ (g)+1/2\ O_2\ (g)=H_2O\ (liq) \qquad (3)$$

$$C_2H_6\ (g)+3\ 1/2\ O_2\ (g)=2\ CO_2\ (g)+3\ H_2O\ (liq) \qquad (4)$$

Because the value of the heat of hydrogenation of ethylene is about 1/2, 1/10, and 1/11, respectively, of the heats of combustion of hydrogen, ethylene, and ethane, it is evident that, in point of the accuracy of the relatively small value of the heat of hydrogenation, the direct method has an advantage of about fifteenfold over the indirect method. This advantage of the direct method, however, is partly counterbalanced by the simpler, purer, and more complete nature of the reaction of combustion as compared with that of hydrogenation. In the case of molecules with four or more carbon atoms, however, the advantage in favor of the direct method for determining the difference in the heats of formation of analogous olefin and paraffin hydrocarbons becomes overwhelmingly large.

In the utilization of the calorimetric data on heats of combustion for the present purpose, one obvious limitation must be made, and that is that in the derivation of any one value for the heat of hydrogenation only the combustion data from one laboratory on all three reactions should be used. The main reason for this procedure is that it helps to eliminate systematic errors in the work of a given laboratory.[3]

II. REVIEW OF THE CALORIMETRIC DATA

There are now available five completely independent sets of calorimetric data yielding values for the heat of hydrogenation of ethylene:

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[1] The report of this work of Rossini and Knowlton will be published, along with other data on the olefine hydrocarbons, in a subsequent number of the Journal of Research of the National Bureau of Standards.

[2] The figures in brackets here and throughout the text refer to the references at the end of the paper.

[3] For example, if only 2 investigators, *A* and *B*, determined all 3 heats of combustion, Q_1, Q_2, and Q_3 independently, there would be 8 possible combinations which could be used to evaluate the heat of hydrogenation; but, of these, the 2 combinations involving AQ_1, AQ_2, AQ_3, and BQ_1, BQ_2, BQ_3 would be expected to be by far the most reliable.

two "old" sets of data on heats of combustion obtained about 50 years ago by Thomsen [3] and by Berthelot and Matignon [4]; two sets of "modern" data on the direct reaction of hydrogenation by Von Wartenberg and Krause [5] and by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan [6]; and one set of "modern" data on heats of combustion obtained at the National Bureau of Standards by Rossini [2] and Rossini and Knowlton [1].

In addition to these five values there is one recently derived by Teller and Topley [7] by a combination of the statistical calculations of the thermodynamic properties of the molecules, hydrogen, ethylene, and ethane, with the experimental data of others on the equilibrium represented by reaction (1). Their procedure in evaluating the heat of hydrogenation is substantially that of utilizing the relation,

$$\Delta H = \Delta F + T\Delta S, \tag{5}$$

where ΔF is the change in free energy, evaluated from equilibrium data, and ΔS is the change in entropy, calculated by statistical methods.

1. DATA OF THOMSEN, 1873–86

Thomsen's [3] data on the combustion of hydrogen and ethane have already been evaluated (see Rossini [2]) and yield $\Delta H° = -68.32 \pm 0.17$ and -368.9 ± 1.3, kilocalories per mole, at 25° C, for reactions (3) and (4), respectively.

Thomsen performed six experiments, two series of three each, on the heat of combustion of ethylene in a flame calorimeter at constant pressure and about 18° C, the amount of reaction being determined from the mass of carbon dioxide formed. By excluding the second experiment of the first series, because its deviation is nearly seven times the average deviation of the remaining five, and converting the data to modern units of energy, there is obtained the value $\Delta H° = -332.9 \pm 0.8$ kilocalories per mole, at 25° C, for reaction (2), the "error" being computed according to Rossini [8]. By combining Thomsen's data for reactions (2), (3), and (4), there is obtained for reaction (1), $\Delta H° = -32.3 \pm 1.5$ kilocalories per mole at 25° C.

2. DATA OF BERTHELOT AND MATIGNON, 1893

The data of Berthelot and Matignon [4] (see also Berthelot [9]) on the combustion of hydrogen and ethane have already been evaluated (see Rossini [2]) and yield $\Delta H° = -68.7 \pm 0.6$ and 372.1 ± 0.8 kilocalories per mole, at 25° C, for reactions (3) and (4), respectively.

Berthelot and Matignon [4] (see also Berthelot [9]) performed three experiments on the combustion of ethylene in a bomb at constant volume and about 14° C. The amount of reaction was determined both from the volume of ethylene burned and the mass of carbon dioxide formed, but the two analytical methods yielded significantly different but random results, the difference being as much as 0.6 percent in one experiment. Corrected to the modern unit of energy, these data yield $\Delta H° = -341.0 \pm 1.6$ kilocalories per mole for reaction (2) at 25° C. By combining the data of Berthelot and Matignon for reactions (2), (3), and (4), there is obtained for reaction (1), $\Delta H° = -37.6 \pm 1.9$ kilocalories per mole at 25° C.

3. DATA OF VON WARTENBERG AND KRAUSE, 1930

The direct hydrogenation experiments of Von Wartenberg and Krause [5] were carried out with a simple calorimetric system consisting of a 0.5-liter rubber-stoppered cylindrical vacuum flask containing the catalyzing solution (400 ml of water with 3 g each of sodium carbonate, gum arabic, and palladium chloride, in colloidal suspension), a Beckmann thermometer, an electrical heating coil, a gas inlet tube terminating in a glass filter plate in the solution near the bottom of the flask, and a gas exit tube above the solution. The hydrogen and ethylene gases were first saturated with water at an unstated temperature, mixed, and then led into the catalyzing solution where the reaction (which was not complete) occurred, presumably at the prevailing room temperature. The effluent gas (hydrogen, ethylene, ethane, and nitrogen) passed out of the reaction vessel carrying an unstated amount of water vapor, through liquid bromine to remove ethylene, through potassium hydroxide to remove bromine vapor, through a cold trap at 0° C to remove ethylene bromide, through potassium hydroxide and calcium chloride, over heated copper oxide in order to oxidize the hydrocarbon to carbon dioxide and water, through calcium chloride to remove water, and then through weighed tubes of soda lime in order to absorb the carbon dioxide, the mass of which determined the amount of reaction. Von Wartenberg and Krause gave no details concerning the evaluation of the electrical-energy equivalent of the calorimeter, except to say that it was determined with electrical energy measured with a voltmeter, an ammeter, and a watch. (Any systematic error in this quantity is directly carried over to the value for the heat of hydrogenation).

These experiments of Von Wartenberg and Krauss were analyzed by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan [6], who pointed out two serious objections to their work, the first one concerning the failure of the experimenters to demonstrate the absence of side reactions, such as irreversible adsorption, and the second (and apparently more serious one) concerning their manner of determining the amount of reaction. The writer has analyzed in detail the latter criticism and finds that the procedure employed by Von Wartenberg and Krause for determining the amount of reaction does leave open the possibility of a systematic error, whose value might conceivably be as large as 10 percent. This calculation confirms the statement of Kistiakowsky and his collaborators that "the ethylene bromide which might remain in the gases (going into the combustion tube) can more than account for the low value for the heat of hydrogenation obtained by Von Wartenberg and Krause."

Von Wartenberg and Krause reported the results of 12 experiments, the average of the first six being 2-percent lower than that of the last six. Making no allowance for possible "unknown" systematic errors, one obtains from the values reported by Von Wartenberg and Krause, $\Delta H° = -30.6 \pm 0.4$ kilocalories per mole, at 25° C, for reaction (1).

4. DATA OF KISTIAKOWSKY, ROMEYN, RUHOFF, SMITH, AND VAUGHAN, 1935

The recent experiments of Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan on the direct hydrogenation of ethylene were carried out with a careful regard for the accuracy of both the calorimetric and the chemical procedures. These experiments were described in detail in the original paper [6], and substantiating experiments were reported in a subsequent paper [10]. The calorimetric method employed was substantially the substitution method [8] wherein the heat evolved by a measured amount of chemical reaction is compared with the heat evolved by a measured amount of electrical energy, using the calorimeter as the absorber and comparator of the two kinds of energy.

The completeness of the reaction of hydrogenation was demonstrated by examination of the reaction products, which showed the absence of ethylene. The possible side reactions were (1) decomposition to form methane, (2) irreversible adsorption on the catalyst, and (3) polymerization plus hydrogenation. Appropriate tests indicated that the effects of the first two reactions, if they occurred at all, were insignificant. A test for the polymerization reaction was deemed not feasible and its existence in any significant amount was considered to be doubtful. As stated by the authors, if this reaction should be shown to occur, the heat of hydrogenation would have to be increased by 0.1 percent for each 0.6 percent of ethylene polymerized, with subsequent hydrogenation, to yield butane.

A possible systematic error, not specifically mentioned by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, would occur if the ethylene contained some ethane. The effect of the presence of ethane as an impurity in the ethylene would be to increase the apparent amount of reaction, as measured by the carbon dioxide from the products of combustion of the effluent gases, without changing the amount of heat evolved, and, consequently, the observed value of the heat of hydrogenation would be lower than the true value by an amount (in percent) equal to the molal percentage of ethane present as an impurity. As stated below, one of the two "good" samples of ethylene used in these experiments undoubtedly contained a significant amount of ethane.

Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan reported the heats of hydrogenation of three different samples of ethylene as follows: (1) a commercial sample, "99.5 percent pure", made from ethyl alcohol; (2) a middle fraction from an extended fractional distillation of the foregoing commercial sample; and (3) a sample, "99.8 percent pure", prepared specially by the Linde Air Products Co., by the fractional distillation of petroleum products. As recommended by the investigators, the data on the commercial sample may be disregarded because of its large amount of impurity, part of which was found to be diethyl ether.

The second sample above was considered to be the purest and the data on it correspondingly best. On this sample there were performed 10 experiments, having an average deviation of 0.10 percent, at an average temperature of 82° C. From the discussion presented by these investigators [6, 10], it would appear that the determination of the electrical-energy equivalent of the calorimeter system had an uncertainty of about 0.10 percent. Assuming an absolute error of ±0.10 percent due to an impurity in the reaction and the determination of the amount of reaction, and computing the errors as before, one finds that the values of these investigators for their "best" sample of ethylene yield $\Delta H° = -32.833 \pm 0.053$ kilocalories per mole for reaction (1) at 82° C.

On the sample of ethylene prepared by Linde from petroleum products, marked "99.8 percent pure", Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan reported the results of four very concordant experiments, which had an average deviation of 0.03 percent. Computing the "error" as before, one obtains $\Delta H° = -32.806 \pm 0.049$ kilocalories per mole for reaction (1) at 82° C. However, in their investigation on the heat of combustion of ethylene, Rossini and Knowlton [1] determined with considerable accuracy the amount of impurity in a sample of ethylene, marked "99.85 percent pure", which had been specially prepared by the Linde laboratory. They found 0.015 ±0.010 mole percent of methane and 0.246 ±0.032 mole percent of ethane. A private communication from the Buffalo laboratory of the Linde Air Products Co. reported that the ethylene prepared for the National Bureau of Standards was from a separate purification and contained slightly less ethane (about 0.05 percent less) than the sample prepared for the Harvard laboratory, both samples having been prepared in 1933. Assuming that the Linde sample of ethylene used by Kistiakowsky and his coworkers contained the same amount of impurity as that given above, one obtains from their data on the Linde sample, when appropriately corrected, the value $\Delta H° = -32.889 \pm 0.050$ kilocalories per mole for reaction (1) at 82° C.

As pointed out by Kistiakowsky and his collaborators, the effect of a possible side reaction of polymerization plus hydrogenation, such as

$$2\ C_2H_4\ (g) + H_2\ (g) = C_4H_{10}\ (g), \tag{6}$$

would be corrected for by increasing numerically the observed values of the heat of hydrogenation by 0.1 percent for each 0.6 percent of ethylene polymerized. That the foregoing is a possible side reaction is evidenced by the free energy calculations recently made by Kassel [12], which yield, for reaction (6) at 82° C, a decrease in free energy of about 4.4 kilocalories per mole of butane. However, in later experiments on the heats of hydrogenation of propylene, butene–1, and heptene–1, Kistiakowsky, Ruhoff, Smith, and Vaughan [10] performed tests to determine the presence of a side reaction of polymerization plus hydrogenation, and reported negative results in tests which would have readily detected 0.5 percent of the hydrogenated polymer in the products of reaction.[4]

The next point to be considered is the reduction from 82° to 25° C of the above two values for the heat of hydrogenation. According to the experimentally determined values of Eucken and Parts [24] on the heat capacities of ethylene and ethane, and the statistical calculations of Eucken and Parts [24] and Smith and Vaughan [11] based upon these data, together with the known accurate values for hydrogen [14, 15], the amount of the reduction from 82 to 25° C may be taken as 0.25 kilocalorie per mole with a possible uncertainty of about ±0.02 kilocalorie per mole. The two values from the work of Kistiakowsky and his collaborators then become, respectively, $\Delta H° = -32.58 \pm 0.06$ and -32.64 ± 0.06 kilocalories per mole for reaction (1) at 25° C.

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[4] An extremely sensitive method of testing for such impurities is the differential vapor-pressure method described by Shepherd [13].

5. DATA FROM THE NATIONAL BUREAU OF STANDARDS, 1931–36

The data obtained at the National Bureau of Standards on the heats of combustion of hydrogen, ethane, and ethylene give the following values of $\Delta H°$ for the respective reactions at 25° C, in kilocalories[5] per mole: reaction (3), Rossini [2], -68.313 ± 0.010; reaction (4), Rossini [2], -372.81 ± 0.11; and reaction (2), Rossini and Knowlton [1], -337.28 ± 0.07. Combination of these values yields, for reaction (1), $\Delta H° = -32.78 \pm 0.13$ kilocalories per mole at 25° C.

III. SUMMARY OF THE VALUES FROM THE CALORIMETRIC DATA

In table 1 are given the values from the five sets of data which have just been reviewed. These are plotted in figure 1. With regard to the half-century-old data of Thomsen [3] and Berthelot and Matignon [4], it would appear safe to conclude that the possibility of systematic errors in their work on heats of combustion is such as to make their values even more uncertain than is indicated by the assigned errors, and that, therefore, the values deduced from their work should be considered as approximations only.

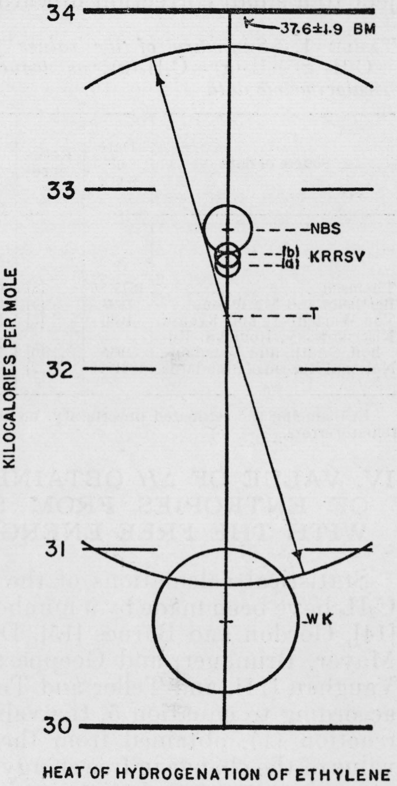

FIGURE 1.—*Plot of the values for the heat of hydrogenation of ethylene, as deduced from the calorimetric data.*

The scale of ordinates gives the value of $-\Delta H°$ at 25° C for the reaction, C_2H_4 (g)$+H_2$ (g)$=C_2H_6$ (g), in kilocalories per mole. The radii of the various circles indicate the estimated uncertainties (not including possible "unknown" systematic errors) of the values from the various sets of data: BM, Berthelot and Matignon [4]; NBS, National Bureau of Standards [1, 2]; KRRSV, Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan [6]; T, Thomsen [3]; WK, Von Wartenberg and Krause [5].

Of the three sets of modern data, the two direct measurements are in complete discord, while the value from the modern data on heats of combustion is in accord with the higher and more recent of the two direct determinations. Because of the care and precautions taken to insure the accuracy of their chemical and calorimetric procedures, and because of the completely different reactions measured, the substantial concordance of the values deduced from the work of Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan [6] at Harvard University and of Rossini [2] and Rossini and Knowlton [1] at the National Bureau of Standards is very gratifying. It would appear that some systematic error, possibly of the nature of those discussed

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[5] See Rossini [8] for a discussion of the unit of energy.

on page 632 existed in the work of Von Wartenberg and Krause [5], and it may be safely concluded, therefore, that the true value of the heat of hydrogenation lies in the immediate neighborhood of the two concordant values from the modern work. There is also a remote possibility, as discussed on page 633 that the values of Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan may be subject to a small correction upward (numerically).

TABLE 1.—*Summary of the values for the heat of hydrogenation of ethylene,* $C_2H_4(g)+H_2(g)=C_2H_6(g)$, *as deduced by the present writer from the various calorimetric data*

Source of data	Date of work	Reference	Reactions measured	Value deduced for $-\Delta H°$ at 25° C	Estimated uncertainty [1]
				Kilocalories per mole	*Kilocalories per mole*
Thomsen	1873–86	[3]	Combustion of H_2, C_2H_4, C_2H_6	32.3	±1.5
Berthelot and Matignon	1893	[4]	Combustion of H_2, C_2H_4, C_2H_6	37.6	±1.9
Von Wartenberg and Krause	1930	[5]	Hydrogenation of C_2H_4	30.6	±0.4
Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan	1935	[6]	Hydrogenation of C_2H_4	(*a*) 32.58 (*b*) 32.64	±0.06 ±0.06
National Bureau of Standards	1931–36	[1,2]	Combustion of H_2, C_2H_4, C_2H_6	32.78	±0.13

[1] In deducing the estimated uncertainty, no allowance has been made for possible "unknown" systematic errors.

IV. VALUE OF ΔH OBTAINED FROM THE COMBINATION OF ENTROPIES FROM STATISTICAL CALCULATIONS WITH THE FREE ENERGY FROM EQUILIBRIUM DATA

Statistical calculations of the entropies of gaseous H_2, C_2H_4, and C_2H_6 have been made by a number of investigators, including Giauque [14], Gordon and Barnes [15], Davis and Johnston [16], Kassel [17], Mayer, Brunauer, and Goeppert-Mayer [18], Frost [19], Smith and Vaughan [11], and Teller and Topley [7]. It is possible to combine, according to equation 5, the value of the change in entropy, ΔS, for reaction (1), obtained from these statistical calculations, with the value of the change in free energy, ΔF, as determined from equilibrium measurements, to obtain a value for the change in heat content, ΔH, for reaction (1).

Teller and Topley [7] (see also Frost [19] and Smith and Vaughan [11]) reviewed the experimental data of Pease and Durgan [20], Travers and Pearce [21], Vvedenskii and Vinnikova [22], and Frey and Huppke [23] on the equilibrium conditions for reaction (1), and deduced a very concordant, and apparently quite reliable, value for the free-energy change for the reaction of hydrogenation at 863° K. Teller and Topley [7] (see also Frost [19], Kassel [17], and Smith and Vaughan [11]) made statistical calculations of values of the thermodynamic function, $(F°-E_0°)/T$, for gaseous C_2H_4 and C_2H_6, combined these with similar values computed for gaseous H_2 by Giauque [14], and obtained a value for the property $(\Delta F°-\Delta E_0°)/T$ for reaction (1). Combination with the "best" value of $\Delta F°$ for 863° K, as obtained from the equilibrium data, then yielded a value for $\Delta E_0°$. To this quantity was added the statistically computed value of $\int_0^{298}\Delta C_p dT$ for reaction (1) to obtain the value for $\Delta H°$ for the reaction of hydrogenation at 298° K or 25° C.

The value thus deduced by Teller and Topley [7] for the heat of reaction (1) was $\Delta H°=-31.05 \pm 0.30$ kilocalories per mole at 25° C. This uncertainty of ±0.30 kilocalorie per mole was considered to be the limit of "probable" error, with the limit of "possible" error being ±0.60 kilocalorie per mole. These limits of error were evaluated by Teller and Topley from a very critical analysis of the fallible factors entering into their calculations, namely: (1), the error in the value of the free energy from equilibrium data; (2), the error in the moments of inertia of ethylene and ethane; (3) the error in the vibrational frequencies of ethylene; (4), the uncertainty in the magnitude of the potential restricting the free rotation of the methyl groups in ethane; and (5), the uncertainty in the vibrational frequencies of ethane. Teller and Topley considered that the possible uncertainties in these quantities were such as to correspond, in the value of $\Delta H°$ at 25° C., in kilocalories per mole, to ±0.10 from (1), to ±0.17 from (2), to ±0.10 from (3), and to ±0.25 from (4) and (5) combined.

As a result of the concordant sets of calorimetric data from Harvard University and the National Bureau of Standards, it appears that the true value for the heat of hydrogenation of ethylene definitely lies from 1.6 to 1.7 kilocalories per mole numerically above the value deduced from the combination of entropies, computed statistically, with the free energy, determined experimentally. Therefore, it must be concluded that, for one or more of the sources analyzed by Teller and Topley [7], the error must greatly exceed what was considered to be the maximum possible.

Assuming that the heat of hydrogenation of ethylene according to reaction (1) is definitely limited to the range $-\Delta H°=32.6$ to 32.8 kilocalories per mole at 25° C., there remain several possible explanations for the discrepancy in the relation (see equation 5) between ΔH determined calorimetrically, ΔS computed statistically, and ΔF determined from equilibrium measurements. This discrepancy has been discussed by Kassel [12] and by Teller and Topley [7], and the possible explanations may be expressed as follows: (1), the experimentally determined equilibrium constants would need to be too large by a factor of about 3; (2), the assigned values for the vibrational frequencies in ethylene or ethane, or both, would need to be in considerable error; and (3), the present calculated difference between the rotational entropies of ethylene and ethane would need to be too large by about 2½ calories per degree per mole. From the many concordant equilibrium data obtained in diverse ways by different investigators, it seems rather improbable that the experimentally determined equilibrium constants can be in error by a significant amount. It appears then that an explanation for the discrepancy must come from the spectroscopic and other molecular data which are utilized in evaluating the rotational and vibrational energy levels of the ethylene and ethane molecules. For example, part or all of the discrepancy may be resolved by appropriately restricting, in the ethane molecule, the rotation of the two methyl groups about the carbon-carbon bond, or by reducing, in the ethylene molecule, the magnitude of the torsional frequency about the carbon-carbon double bond.

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