199. *On the Equilibrium and the Heat of the Reaction* $C_2H_4 + H_2 = C_2H_6$.

By Eduard Teller and Bryan Topley.

1. *Introduction.*

A statistical-mechanical calculation of the equilibrium constant $K_p = P_{C_2H_6}/P_{C_2H_4} . P_{H_2}$ has been carried out by Frost (*Compt. rend. U.R.S.S.*, 1933, **161**), who obtained agreement with the experimental results then known, the difference between theory and experiment being 15% at 700° Abs., rising to 25% at 1000° Abs. Since the appearance of his work new experimental data have been published for the equilibrium and for the reaction heat, and also for one of the inertial moments of ethylene. Repeating the calculation with the newer data, we find a much greater discrepancy, the calculated value of K_p being 2·43 times larger than the experimental value at 863° Abs. This change results mainly from the difference between the newer value for the reaction heat ($-\Delta H = 32{,}575 \pm 50$ cals. at 298° Abs.) obtained by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan (*J. Amer. Chem. Soc.*, 1935, **57**, 65) and the earlier value of 30,630 ± 300 found by von Wartenberg and Krause (*Z. physikal. Chem.*, 1930, *A*, **151**, 105). The calculation is more sensitive to changes in the reaction heat than in the other quantities involved, and it appears that rather a large change in some of the molecular constants would be required in order to remove the discrepancy now revealed.

For reasons given in Section 3, it seems to us that the newer equilibrium measurements by Travers and Pearce (*J. Soc. Chem. Ind.*, 1934, **53**, 322; also Travers and Hockin, *Proc. Roy. Soc.*, 1932, *A*, **136**, 1) cannot be rejected. On the other hand, some of the molecular constants (*viz.*, the forces acting between the methyl groups in ethane, some of the inertial moments, and some of the vibration frequencies) are known only by indirect methods. Very detailed consideration is necessary in order to decide what uncertainty is thereby introduced into a statistical mechanical correlation of the heat of reaction determined at the ordinary temperature and the equilibrium constant determined at relatively high temperatures.

Our main object is to investigate whether such a choice is possible of those constants which are not known exactly as will reconcile the thermal data of Kistiakowsky *et al.* with the equilibrium data. To this end we have calculated an upper limit for the reaction heat by making certain (maximum) assumptions concerning such of the frequencies in the ethylene and ethane molecules as are not fixed spectroscopically, and concerning the potential energy of the restricted rotation of the methyl groups in ethane. These assumptions are the most extreme which we believe to be possible within the limits set by the spectroscopically observed frequencies and the measured specific heats.

The conclusion from the calculation is that, if we accept the equilibrium data within limits of error suggested by a consideration of all the measurements (see Section 3), then the reaction heat must lie at least 900 cals. below the lower limit allowed by Kistiakowsky and collaborators.

The heat of reaction which we derive from the absolute value of the equilibrium constant by means of the most probable values of the molecular constants (see Section 2) is $-\Delta H = 31{,}050 \pm 300$ cals. per mol. at 298° Abs.*

2. *The Partition Functions.*

The equilibrium constant of the reaction $C_2H_4 + H_2 = C_2H_6$, if the participants are treated as perfect gases, is given by:

$$K_p = 1{\cdot}0132 \times 10^6 (kT)^{-1} G_{C_2H_6}/G_{C_2H_4} \times G_{H_2}$$

---

* This is somewhat higher than the value of von Wartenberg and Krause, but not in actual disagreement with it. We lay less stress upon this than upon the definite contradiction with the more recent heat measurements, which claim a much greater accuracy than the older; Kistiakowsky and collaborators (*loc. cit.*) have pointed out that there is a possible source of systematic error in the work of von Wartenberg and Krause, which would make their results too low. But it is also quite possible (see Section 4) that the error in question was unimportant, and there is some evidence for this in the detailed results, although the point is uncertain.

where K_p is expressed in atmospheres, k is the Boltzmann constant, T the absolute temperature, and the numerical factor converts absolute pressures into atmospheres; G is the partition function (the volume being omitted) for the species indicated. Apart from the special case of hydrogen, the partition functions (see Fowler, "Statistical Mechanics," 1929, p. 106) above room temperature break up into factors of simple form for translation, rotation and vibration, internal rotation of the methyl groups in ethane, nuclear spin, and the Boltzmann factor for the energy of the molecule in its lowest state referred to the free atoms as the zero of energy. The three Boltzmann factors give a term $e^{-\Delta E_0/RT}$, where $-\Delta E_0$ is the heat of reaction at absolute zero; this is the quantity we are primarily concerned with in the present calculation. The products of the simple factors referred to have to be divided by the appropriate symmetry numbers, which are 18 for ethane, 4 for ethylene, and 2 for hydrogen.

It is not necessary to give all the details of the calculation of the equilibrium constant; there are no essential omissions in the calculation given by Frost (*loc. cit.*). We shall treat, as Frost did, the internal rotation in ethane as a free rotation, and include it in the rotational factor of the partition function; in addition, we shall introduce the correction taking account of the potential energy of interaction of the rotating methyl groups.

For hydrogen, we have the very accurate computation by Giauque (*J. Amer. Chem. Soc.*, 1930, **52**, 4816) from spectroscopic data of the function $-(F^\circ - E_0{}^\circ)/T$ (where F° is the molar free energy at 1 atm. pressure and $E_0{}^\circ$ the energy at absolute zero). This function is related to the partition function G_{H_2} by

$$\log_e G_{H_2} = \frac{1}{R}\left\{-\frac{F^\circ{}_{H_2} - E_0{}^\circ{}_{H_2}}{T} - \log_e kT + \log_e (1{\cdot}0132 \times 10^6)\right\}$$

The factors in the partition functions of ethylene and ethane depend in the following way upon the molecular constants. The translational factors involve only the molecular weights and require no special discussion, and the nuclear spin factors cancel automatically.

The rotational factor for ethylene is proportional to $(I_A I_B I_C)^{\frac{1}{2}}$. The moments of inertia $(\times 10^{40})$, $I_A = 5{\cdot}7$, $I_B = 27{\cdot}5$, $I_C = 33{\cdot}2$, have recently been published by Badger (*Physical Rev.*, 1934, **45**, 648) on the basis of measurements of the photographic infra-red spectrum (Bonner, unpublished) and of the rotational Raman effect (Lewis and Houston, *ibid.*, 1934, **44**, 903). The values assumed by Frost were $I_A = 3{\cdot}80$, $I_B = 27{\cdot}0$, $I_C = 31{\cdot}0$, on the basis of an earlier spectroscopic determination by Badger and Binder (*ibid.*, 1931, **38**, 1442); these give a value of $(I_A I_B I_C)^{\frac{1}{2}}$ 1·28 times smaller than Badger's new spectroscopic values. So far, only a preliminary announcement by the latter has appeared (*loc. cit.*), but the moments of inertia agree with what would be anticipated from a model of the ethylene molecule, and there seems to be no reason to suppose that any important error enters here. Furthermore, as Badger points out, some confirmation is obtained from the corresponding moment of inertia for the molecule $CH_2{:}O$ ($I_A = 2{\cdot}941$) obtained by Dieke and Kistiakowsky (*ibid.*, 1934, **45**, 4) from the electronic band system, which is in as good agreement as is to be expected with one-half the figure for ethylene.

For ethane, the factor which takes account both of the rotation of the molecule as a whole and of the relative rotation of the methyl groups is proportional to $I_A I_C$, where I_A is the inertial moment of one methyl group round the axis through the carbon atoms, and I_C is that of the whole molecule round the principal axis perpendicular to the C–C bond. No direct determinations have been made of I_A or I_C, so they have to be derived by inference from other compounds or from a model. For I_A we have the following information. The value for methane is 5·4, with an uncertainty less than 0·1 according to Teller ("Hand- und Jahrbuch der chemischen Physik," Vol. IX, Part 2, pp. 134, 156), who gives two methods of calculation. The first depends on a comparison of the Raman and infra-red spacings for a single methane band, and the second on a comparison of the spacings for the different infra-red bands.* The values for the four methyl halides vary from 5·6 to 5·4. The

* The figure derived by the second method is wrongly given in this article owing to a numerical error. The same applies to the corresponding figure for the methyl halides. The error was observed by Dennison and Johnston, and we are indebted to Mr. W. G. Penney for communicating to us their revised result, which we use later in this section.

deviations from the value 5·4 for methane, although only slightly exceeding the possible error, are probably real, and may be understood as being caused by an attraction between the halogen and hydrogen atoms. There is a similar effect in the case of formaldehyde and ethylene, as may be seen from the figures given above. We therefore consider that the value of I_A for one methyl group in ethane may be taken as 5·4 ± 0·1, and we have actually used $5{\cdot}37 \times 10^{-40}$ to facilitate comparison with the results given by Frost (*loc. cit.*), who deduced this figure from a model.

To calculate I_C we may reasonably assume that the methyl groups have the same configuration as in methane. The C–C distance is 1·52 ± 0·05 Å. (Wierl, *Ann. Physik*, 1931, **8**, 521; 1932, **13**, 453). Hence we obtain $I_C = 40{\cdot}09 \times 10^{-40}$, which is also the value used by Frost.

The possible error in the rotational factor for ethylene is ± 2%, and for ethane ± 7%. The possible error in the partition function coming from the rotational factors alone may therefore be taken as ± 10%.

The vibrational contribution to the partition function of a molecule consists of the product of terms of the form $[1 - e^{-h\nu_i/kT}]^{-1}$, where the ν_i are the frequencies of the normal modes of vibration.* The most probable values of the frequencies of these vibrations are discussed in detail in the following paper. For ethylene they are (in wave-numbers) 3240, 3110, 3019, 2990, 1623, 1444, 1342, 1160, 1110, 1097, 950, and 730. Of these, the frequencies 1160, 1110, 1097, and 730 are known with much less certainty than the others. The effect of this uncertainty upon the calculation is considered in Section 6, but we remark here that although Frost used three frequencies different from ours (950, 950, and 940 instead of 1160, 1110, and 730) the difference made by this in the partition function is only a factor of 1·017 at 863° Abs. The product of the twelve vibrational factors in the partition function is approximately 4 in the temperature range of the experiments.

Ethane has five non-degenerate frequencies, for which the most probable values (see following paper) are 3020, 2955, 1460, 1370, and 993, and six two-fold degenerate frequencies for which the most probable values are 2899, 2890, 1480, 1460, 827, and 750. The three frequencies at 1460, and especially the frequency at 750, are uncertain, and the effect of this uncertainty upon the calculation is considered in Section 6. The product of the seventeen vibrational factors in the partition function for ethane is of the order of magnitude 8 in the temperature range in question. The value we obtain at 863° Abs. differs from that of Frost by a factor of 1·036.

3. *The Equilibrium Constant.*

Four investigations of the equilibrium have been published, covering between them a range of 300° and of over 1000-fold in K_p. All the data are assembled in the following table.

Col. 1 indicates the source of the data: PD = Pease and Durgan (*J. Amer. Chem. Soc.*, 1928, **50**, 2715); TP = Travers and Pearce (*loc. cit.*); VV = Videnski and Vinikova (*J. Gen. Chem., Moscow*, 1934, **4**, [46], 120); FH (a) = Frey and Huppke (*Ind. Eng. Chem.*, 1933, **25**, 54); FH (b) = reinterpretation of these results by Kistiakowsky *et al.* (*loc. cit.*).

Col. 2 shows the absolute temperatures, and col. 3 the experimental conditions: E means that a gaseous mixture prepared to have approximately the equilibrium composition was heated in a silica bulb without added catalyst—conditions under which the reaction is known to proceed largely in the gas phase (see Pease, *J. Amer. Chem. Soc.*, 1932, **54**, 1878; Marek and McCluer, *Ind. Eng. Chem.*, 1931, **23**, 878, where other references are given; Rice and Dooley, *J. Amer. Chem. Soc.*, 1933, **55**, 4245); the letters D and C indicate that the equilibrium was reached starting with ethane or with ethylene plus hydrogen, respectively; H refers to a special set of experiments by Travers and Pearce (*loc. cit.*; Table VII), in which the gas mixtures were roughly of the equilibrium composition initially as in the experiments marked E, but the partial pressure of hydrogen was very much larger. The equilibrium constants which we have calculated from the data of this table (Table VII)

---

* The tables of C_v (Einstein formula) in Landolt–Börnstein, " Physikalisch-Chemische Tabellen," 5th Edn., and in Nernst's " The New Heat Theorem," English Edn., are incorrect in a number of places, especially at $\beta\nu/T$ = 1·1, 1·2, 8·5, 8·9, 9·0.

1. Ref.	2. Temp., Abs.	3. Exptl. method.	4. No. of expts.	5. $\log_{10} K_p$ in atms.	6. $- \Delta E_0$.	7. $\log_{10} K_p$, calc.
PD	973°	E	4	0·699	29,490	0·684
TP	923	H	2	1·105	29,530	1·079
PD	923	E	2	1·086	29,450	1·079
TP	903	H	5	1·268	29,500	1·249
TP	893	E	31	1·351	29,480	1·337
TP	883	H	6	1·438	29,470	1·427
TP	883	E	9	1·445	29,490	1·427
PD	873	E	4	1·509	29,380	1·519
TP	863	H	3	1·618	29,440	1·613
TP	863	E	46	1·613	29,420	1·613
TP	863	D; SiO_2	5	1·614	29,420	1·613
TP	843	E	5	1·815	29,450	1·808
TP	843	D	12	1·779	29,280	1·808
TP	823	E	3	(2·131)	(29,860)	2·013
FH (a)	773	D; Cr_2O_3	2	2·495	29,160	2·569
FH (b)				2·620	29,600	
VV	773	C; Cr_2O_3	1	2·50	29,180	2·569
VV	773	D; Cr_2O_3	1	2·50	29,180	2·569
FH (a)	723	D; Cr_2O_3	2	3·119	29,150	3·201
FH (b)				3·252	29,500	
FH (a)	673	D; Cr_2O_3	2	3·824	29,110	3·927
FH (b)				4·086	29,910	

are remarkably consistent. The use of a catalyst is indicated explicitly in col. 3; SiO_2 refers to experiments in which the bulbs were packed with silica tubing. The experiments below 800° were done by a flow method, the flow speed being varied as the criterion of equilibrium.

Col. 4 gives the number of experiments * averaged in finding the equilibrium constants given in col. 5. Col. 6 contains values of the energy decrease in the reaction at absolute zero. These are calculated by inserting into the partition functions † of ethane and ethylene the values of the molecular constants given in Section 2, and combining the results with the free energy of hydrogen as calculated by Giauque (*loc. cit.*).

The most reliable result for the equilibrium constant is $\log_{10} K_p = 1{\cdot}613$ at 863° Abs., since more experiments were done at this than at any other temperature. We take $- \Delta E_0 = 29{,}420$ cals. per mol. as the most probable value for the heat of reaction at absolute zero, with a possible uncertainty of $\pm$ 100 arising from experimental error in K_p. This figure is the basis from which we have calculated the heat of reaction $- \Delta H_{298°} = 31{,}050$.

The concordance of the experiments at different temperatures can be assessed by comparison of the values of $- \Delta E_0$ in col. 6, or the values for $\log_{10} K_p$ in col. 7, which are obtained by calculating the change in free energy at each temperature with $- \Delta E_0 = 29{,}420$, and taking the most probable values for the molecular constants. Corresponding to an uncertainty of $\pm$ 100 cals. in $- \Delta E_0$, the error in $\log_{10} K_p$ is about $\pm$ 0·025.

It is clear from the experimental results on the equilibrium constants, as presented in the papers referred to, that the experimental quantity $P_{C_2H_6}/P_{C_2H_4}P_{H_2}$ does reach and maintain a constant value. There are, however, simultaneous irreversible reactions producing methane and more complex hydrocarbons. The possibility therefore comes into question that this quantity merely takes on an approximately stationary value through an accidental balancing of the rates of removal of the three substances in the irreversible reactions;

---

* In the case of the experiments by method E, we have entered the number of experiments for which details are given in Table I of the paper of Travers and Pearce. Professor Travers informs us that the averaged values of K_p for experiments by this method, given in Table X, are derived from a larger number of experiments than those detailed in Table I. We have entered in col. 5 the averaged values given by Travers and Pearce.

Pease and Durgan found that 823° was too low a temperature for the attainment of equilibrium in the homogeneous reaction; the results of Travers and Pearce at this temperature are not in good accord with their results at higher temperatures; we have therefore omitted the value 2·131 in col. 5 from further consideration.

† Small corrections to these values of ΔE_0 are required on account of the effects discussed in Section 5.

the true equilibrium ratio might then be seriously different from this stationary value. This possibility is excluded by the combined weight of the following considerations. First, the numerous experiments of Travers and Pearce on the homogeneous reaction at 863° and 893° include a range of 100-fold in the initial ethylene pressures and 20-fold in the initial hydrogen pressure; the results show no detectable dependence upon these changes. The kinetic studies by Pearce and Travers (*loc. cit.*) of the progress of the side reactions show that the rate of formation of methane depends on the partial pressures of ethylene, ethane, methane, and hydrogen, and the rate of formation of complex hydrocarbons is proportional to the square of the ethylene pressure. There is thus no likelihood of the stationary state simulating an equilibrium over so wide a range of relative pressures of ethylene and hydrogen. Secondly, the temperature dependence of such a pseudo-equilibrium could only by a very improbable coincidence agree at all closely with that of a true equilibrium, whereas in fact the experimental values of $\log_{10} K_p$ vary with temperature in the quantitative manner predicted by the absolute statistical mechanical calculation for the true equilibrium. Thirdly, the results obtained by the catalytic methods (here the results of Videnski and Vinikova, in which equilibrium was reached from both sides, are particularly significant) agree with those obtained without catalysts, and this again is only intelligible if true equilibrium is obtained by both methods.

Independently of the statistical mechanical calculation of the reaction heat at any temperature through the intermediate calculation of $-\Delta E_0$, we can, of course, derive a purely thermodynamic value from the relationship $-\Delta H_T = R \,.\, d \log_e K_p/d(1/T)$. In the present instance the substitution, for practical purposes, of the difference quotient $\delta \log_e K_p/\delta(1/T)$ for the differential coefficient is admissible, since the heat capacities of reactants and products are almost equal in the temperature range of the experiment (ΔC_p for $C_2H_4 + H_2 = C_2H_6$ has the following value in cals. per mol.: at 973° Abs., $-0{\cdot}167$; at 863°, $-0{\cdot}671$; at 673°, $-1{\cdot}760$. These are calculated with the most probable value of the vibration for ethylene and ethane, and the figure 4150 for hydrogen).

We should *a priori* prefer the thermodynamic to the statistical-mechanical method because the moments of inertia do not enter into the former.* Kistiakowsky and collaborators (*loc. cit.*), considering only the experiments of Pease and Durgan and Frey and Huppke, found that $-\Delta H$ (in the temperature region of the experiments) is changed from 31,100 to 33,900 by their reinterpretation of the latter workers' data. This situation is improved by giving a reasonable weight to the numerous newer experiments. Nevertheless, since the more accurate values of K_p are concentrated in a relatively small temperature range, the uncertainty in the difference quotient $\delta \log_e K_p/\delta(1/T)$ remains some 3 or 4 times greater than the uncertainty in the statistical mechanical calculation. We therefore give no weight to the thermodynamic method.

4. *The Calorimetric Data.*

The only direct determinations (by catalytic combination of the gases in the calorimeter) are the two mentioned at the beginning of this paper. Kistiakowsky and his co-workers' measurements were done with a highly developed calorimetric technique, and the reproducibility of the results was such that the " accidental " error could be given as ± 50 cals. Great precautions were taken to ensure purity of the ethylene. The probable sources of " systematic " error are discussed in some detail by the authors, and we are unable to see any omission in their discussion. We are therefore left with an unexplained discrepancy between this determination and the equilibrium measurements.

Von Wartenberg and Krause (*loc. cit.*) used as a catalyst in the calorimeter a palladium sol through which the mixed gases were bubbled after expansion through a porous plug. Part of the ethylene was hydrogenated, the remainder being absorbed by bubbling the

---

* It happens that the uncertainty in the molecular frequencies affects the extrapolation of the thermodynamic value down to 298° to about the same extent as it affects the statistical mechanical calculation of $\Delta E_0 + \int_{0^\circ}^{298^\circ} \Delta C_p \,.\, dT$, so that in this respect no advantage attaches to the thermodynamic method.

gases through a sloping tube 30 cm. long containing liquid bromine. Professor von Wartenberg has provided us with more detailed information about the conditions of his experiments, and has kindly calculated for us the corrections required on account of the volume and pressure changes of the water-vapour-saturated gases and the Joule–Thomson cooling of the ethylene passing through the porous plug. The net effect of these corrections is to lower the reaction heat slightly. Kistiakowsky and collaborators attribute the difference of 2000 cals. between their own result and that of von Wartenberg and Krause to the fact that ethylene bromide has a vapour pressure of 3·5 mm. at 0°, so that the ice-cooled trap used to remove ethylene bromide from the gas stream (before it was analysed for ethane by combustion to carbon dioxide) would not be adequate. This is, of course, correct; but since von Wartenberg and Krause state that blank experiments showed that all the ethylene was removed from the gas stream by the bromine tube, whereas ethylene bromide vapour, like ethylene, would have been burnt and weighed as carbon dioxide, we conclude that the ethylene bromide must have been effectively held in the liquid bromine because of its high solubility. It is therefore not necessary to reject the value obtained by von Wartenberg and Krause, although the limits of error may be a little higher than ± 300 cals. suggested by these authors.

We state here for completeness the value which can be calculated from existing data on the heats of combustion. Rossini (*Bur. Stand. J. Res.*, 1931, **6**, 1; **7**, 329) has recalculated the earlier determinations of the heat of combustion of hydrogen, with the following results (cals. per mol. H_2, at 25° and 1 atm. pressure): Schuller and Watha, 68,331; Thomsen, 68,324; Mixter, 68,309. His own determination gave 68,313 ± 10. For ethylene, the only published result on which any reliance can be placed is that of Thomsen. According to Kharasch's recalculation (*ibid.*, 1929, **2**, 359), the figure is 331,600 cals. Rossini (*ibid.*, 1934, **12**, 735) recalculated Thomsen's result (at 15°) for ethane, finding 368,900 ± 1300, and Berthelot and Matignon's result, finding 372,100 ± 800, whereas his own determination gave 372,810 ± 110 cals. at 25°. Hence, according as we take Rossini's or Thomsen's value for ethane, the heat of hydrogenation of ethylene is 27,100 or 31,000 respectively. It is evident that no certain conclusion can be drawn from these heats of combustion.

5. *Minor Factors affecting the Partition Functions of Ethylene and Ethane.*

The experimental evidence (from specific-heat data) for the magnitude of the restriction on the rotation of the methyl groups in ethane is reserved for the succeeding paper, because the vibration frequencies of ethane cannot be discussed independently of the internal rotation. We have now to consider the correction to the partition function of ethane required on account of this restriction.

At temperatures high enough for several quantum states of the restricted rotator to be excited, the factor in the partition function is the mean value $\overline{e^{-(\varepsilon_P - \varepsilon_0)/RT}}$ averaged over a complete rotation; ε_0 is the zero-point energy (per mol.) of the restricted rotation; ε_P is the potential energy taken as a function of the displacement angle ϕ from the symmetrical position in which one methyl group goes over into the other by reflexion in the plane α (see following paper). This expression results from substituting the classical integral taken over the whole range of the co-ordinates and momenta for the quantum mechanical sum over all states. The zero-point energy enters into the classical expression because it is the level from which the energy must be measured in order to be consistent with the definition of ΔE_0 (see Section 2).

If the further condition is fulfilled that $RT \gg \varepsilon_P - \varepsilon_0$, then $\overline{e^{-(\varepsilon_P - \varepsilon_0)/RT}}$ can be replaced by $e^{-\overline{(\varepsilon_P - \varepsilon_0)}/RT}$ where $\overline{\varepsilon_P - \varepsilon_0}$ is the mean value, averaged over a complete rotation, of $\varepsilon_P - \varepsilon_0$.

Clearly, the factor $\overline{e^{-(\varepsilon_P - \varepsilon_0)/RT}}$ affects the equilibrium constant K_p to the same extent as, but in the opposite sense to, an increase $\overline{\varepsilon_P - \varepsilon_0}$ in the absolute value $|\Delta E_0|$. Therefore, since the restriction on the rotation was not introduced in the calculation of $-\Delta E_0$, the values of this quantity given in Section 3 are too small by the amount $\overline{\varepsilon_P - \varepsilon_0}$.

If we consider temperatures high enough for the sum of states to be replaced by the classical integral, the alteration in the energy content required to take account of the restriction upon the rotation is equal to $\overline{(\varepsilon_P - \varepsilon_0)\, e^{(\varepsilon_P - \varepsilon_0)R/T}}$. If, in addition, $RT \gg \overline{\varepsilon_P - \varepsilon_0}$, the exponential factor can be omitted, and we are left with $\overline{\varepsilon_P - \varepsilon_0}$. This extra heat content of ethane operates to lower the heat of reaction $|\Delta H|$.

Thus, if both the equilibrium constant and the reaction heat are considered at sufficiently high temperatures, the relation between these two quantities is unaffected by the restriction upon the internal rotation of ethane.

It was assumed by Teller and Weigert (*Nachr. Ges. Wiss. Göttingen*, **1933**, 218) that ε_P is of the form $a \cos 3\phi$; this is a reasonable model of the rotator if the restricting potential is not large; in any case, as is shown in the paper referred to, qualitatively the same result is obtained even with a very different form of potential. The low-temperature specific-heat measurements of Eucken and Weigert (*Z. physikal. Chem.*, 1933, *B*, **23**, 265) were best fitted with $a = 160$ cals. This corresponds to $\overline{\varepsilon_P - \varepsilon_0} = 40$ cals. The condition $RT \gg \overline{\varepsilon_P - \varepsilon_0}$ is fulfilled for the temperature range of the equilibrium measurements, and therefore a correction of $+ 40$ cals. should be made to the calculated values of $- \Delta E_0$.

The temperature 298° for which we have calculated $- \Delta H$ is not quite high enough for application of the approximation that the extra energy content of ethane is $\overline{\varepsilon_P - \varepsilon_0}$; by integrating graphically the specific heat curves of the restricted rotator given by Teller and Weigert (*loc. cit.*), we estimate the extra energy content to be 30 cals. Consequently, the error in $|\Delta H_{298^\circ}|$ made by omitting from our calculations all effects due to the restriction on the rotation is about $- 10$ cals. only.

In our calculations we treated all the rotational degrees of freedom of ethylene and ethane as classical. By omitting the quantum corrections for very low temperatures, an error of approximately $+ 10$ cals. is made in $|\Delta E_0|$, but no error in $|\Delta H_{298^\circ}|$, since a cancellation of the same kind as the one discussed above, but in this case more complete, takes place here also.

The other minor factors omitted from the calculation are: the change of the inertial momenta of ethylene and ethane in the higher rotational and vibrational levels; the anharmonicity of the vibrations; the deviations from the ideal gas laws. These effects are of the order of 1% or less in the equilibrium constant, and to the accuracy we are concerned with, we may neglect them.

6. *Limits of Possible Error in the Calculation of the Reaction Heat.*

Experimental error in the equilibrium measurements leads to a possible uncertainty in the derived value of ΔE_0 amounting to ± 100 cals. (see Section 3). In addition, the calculation of ΔE_0 and ΔH_{298° from the value of K_p at 863° is subject to whatever error arises from our incomplete knowledge of the molecular constants of ethylene and ethane. The possible error in the partition function ratio arising from the uncertainties in the moments of inertia is $\pm 10\%$ (see Section 2).

The possible limits in the case of the vibration frequencies cannot be so simply stated. The situation with respect to the calorimetric measurements (outlined in Section 4) makes it important to obtain an upper limit to the value of $|\Delta H_{298^\circ}|$ which shall be consistent with the equilibrium data, the measured specific heat, and the spectroscopically known frequencies. We therefore discuss this upper limit rigorously, starting with the uncertain frequencies of ethylene.

It will be seen from the discussion in the following paper that the four frequencies to which we assigned the values 730, 1097, 1110, and 1160 can be considerably changed (subject to certain conditions) without contradicting accepted data. No material uncertainty arises from the other frequencies. It is clear that we need only consider such changes as do not lead to a specific-heat curve lying outside the limits of error of the measurements, *i.e.*, $\pm 1\%$. Since we are concerned to find an upper limit to the reaction heat, we have examined the effect of the following hypothetical changes, designed to raise the value of the partition function of ethylene to the greatest possible extent: (1) In the range of the experiments (178·6—464° Abs.) a specific heat curve lying 1% above the measured values is used. (2) The four frequencies are replaced by a single four-fold frequency so chosen that at 464° Abs. the upper possible limit of the specific heat is reproduced. It can be shown[*] that this four-fold frequency gives a more rapid rise of the specific heat with increasing temperature than any other possible choice. (3) The four frequencies are replaced by three frequencies equal to infinity and one so chosen that the upper possible limit of the measured specific heat is reproduced at 178·6° Abs. It can be shown[*] that this gives a slower fall of the specific heat with decreasing temperature than any other possible choice.

If therefore we extrapolate the specific-heat curve described in (1) from 464° Abs. to 863° Abs. by means of the four-fold frequency, and from 178·6° Abs. to 0° Abs. by means of the single frequency, we obtain a specific-heat curve which certainly lies higher than the real curve at all temperatures; and since the logarithm of the partition function at temperature T is related to the specific heat curve through a term $+\int_0^T \frac{dT}{T^2}\int_0^T C\,.\,dT$, where C is the molar heat capacity, it is clear that the hypothetical specific-heat curve gives an upper limit for the vibrational factors in the partition function of ethylene.

By this calculation we find that the partition function of ethylene cannot be raised by more than 6% above the value corresponding to the vibration frequencies given in Section 2.

For ethane we have to consider what changes are possible in the vibration frequencies[†] which *decrease* the partition function. The frequencies not determined with certainty spectroscopically are ${}^2\nu_a^{M} = 750$, ${}^2\nu_a^{CH_3} = 1460$, and $\nu_t^{CH_3} = 1460$. All other frequencies are known with a high degree of probability.

The main cause of uncertainty is the restriction on the internal rotation of the methyl groups, which we have taken as equivalent to a variation of potential energy of 320 cals. during the rotation. The supposition that this restricting potential is larger has two consequences of importance. First, the partition function is decreased (see Section 5). Secondly, except at very low temperatures, the contribution to the specific heat of ethane coming from the internal rotation is increased (see Teller and Weigert, *Nachr. Ges. Wiss. Göttingen*, 1933, 218), and since the specific heat is experimentally known with an accuracy of 1% in a certain temperature range, the uncertain frequencies must be raised sufficiently to produce a compensating reduction in the specific heat. This causes a further decrease in the partition function.

---

[*] The general problem which we have to consider is as follows: given a set of frequencies which are subject to the condition that they give rise to a definite vibrational heat capacity at one temperature T_1, what further conditions are necessary in order that the vibrational heat capacity at a different temperature T_2 shall take an extreme value (a maximum or a minimum)? It is proved below by a variational argument that an extreme value is possible only if all frequencies in the set considered which are neither zero nor infinite are equal. Out of these possibilities we have to select by trial those which make the heat capacity an absolute maximum. It can easily be verified that the procedures (2) and (3) specified above do give the required maxima for $T_2 > T_1$ and $T_2 < T_1$ respectively.

The proof by the variational calculus is as follows: Let $C(\nu/T)$ be the heat capacity of a vibrational degree of freedom with frequency ν. We require the condition that $\sum_n C(\nu_n/T_2)$ shall have an extreme value, under the restriction that $\sum_n C(\nu_n/T_1)$ has a fixed value. Putting the variation in ν_n equal to $\delta\nu_n$ and $\partial C(\nu_n/T)/\partial\nu_n$ equal to $C'(\nu_n/T)$, the variations of the two sums will be

$$\sum_n C'(\nu_n/T_2)\delta\nu_n \quad . \quad . \quad . \quad . \quad . \quad (a) \qquad\qquad \sum_n C'(\nu_n/T_1)\delta\nu_n \quad . \quad . \quad . \quad . \quad . \quad (b)$$

A necessary condition for the extreme value we require is that the sum (a) shall be zero for all variations $\delta\nu$ such that the sum (b) is zero. In the theory of variations it is shown that there exists a constant a such that $\sum_n [C'(\nu_n/T_2) - aC'(\nu_n/T_1)]\delta\nu_n = 0$ for all possible sets of $\delta\nu_n$. Therefore each of the terms in the bracket must vanish separately, so that $C'(\nu_n/T_2)/C'(\nu_n/T_1) = a$. If $C(\nu/T)$ is the Einstein specific heat function, it can be shown that

$$C'(\nu_n/T_2)/C'(\nu_n/T_1) \neq C'(\nu_m/T_2)/C'(\nu_m/T_1)$$

if ν_n and ν_m are unequal and neither of them is equal to zero or infinity. Therefore $\sum_n C(\nu_n/T_2)$ can only have the extreme value required if all frequencies not equal to zero or infinity are the same.

[†] The statements made in this section about vibration frequencies are based upon the detailed discussion in the following paper, where also the notation used to describe the vibrations is explained.

The lower limit to the partition function is obtained as follows. We first find the heat capacity of the internal rotation, assuming the highest acceptable value for the restricting potential, and add to this the ordinary rotational and translational heat capacity and the heat capacity contributed by the frequencies which are definitely known spectroscopically. By subtracting this sum from a value 1% lower (*i.e.*, the reverse of the procedure for ethylene) than the measured heat capacity at any temperature, we obtain the minimum heat capacity to be attributed to the uncertain frequencies; this is done for the highest and lowest temperatures of the measurements of Eucken and Parts (*Z. physikal. Chem.*, 1933, *B*, **20**, 184). The extrapolation up to 863° Abs. and down to 0° Abs. is then done by a principle analogous to that adopted for ethylene. For the extrapolation upwards, this means putting as many frequencies as possible equal to infinity. It is not actually necessary to make quite so extreme an assumption, since there are certain restrictions upon the uncertain frequencies: the ν_a^M vibration must be the lowest of these, and it is degenerate; and the three ν^{CH_3} frequencies cannot lie higher than about 1500. Accordingly, we have assumed a three-fold frequency of 1500. The value, then, to be assumed for the $^2\nu_a^M$ frequency depends upon the simultaneous assumption made about the restricting potential. It is also clear that the ν^{CH_3} frequencies are in any case too high to influence the extrapolation down to 0° Abs., so that in this region only $^2\nu_a^M$ is of importance.

We have carried through a calculation of the lower limit for the partition function of ethane, taking the potential restricting the internal vibration to be 525 cals. This we consider to be a safe margin over that found experimentally by Eucken and Weigert (315 ± 60) (*Z. physikal. Chem.*, 1933, *B*, **23**, 265) and estimated theoretically as 350 by Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 3191). The direct result of introducing the restricting potential is to lower the partition function by 5·8% as compared with the free internal rotator. The concomitant extreme assumption about the uncertain frequencies produces a further decrease of 11·8%. The total change of 18·3% corresponds to an increase of 290 cals. in $|\Delta E_0|$ for the reaction, and to an increase of 250 cals. in $|\Delta H_{298^\circ}|$. The 40 cals. difference is due to the effect upon the heat capacities, in the range 0—298° Abs., of the restricting potential and the changes in the frequencies.

If we now assume that all uncertainties act to the fullest extent in the direction of raising the calculated reaction heat $|\Delta H_{298^\circ}|$, we find that the total (maximum) uncertainty is 620 cals., made up as follows: experimental error in the equilibrium constant, 100 cals.; from the rotational part of the partition function ratio, 170 cals.; from the vibrational part of the partition function of ethylene, 100 cals.; from the restricted internal rotation and the vibrational part of the partition function of ethane, 250 cals. Thus, the upper limit to the reaction heat is $-\Delta H_{298^\circ} = 31{,}670$ cals. This leaves a difference of 900 cals. from the calorimetric determination of Kistiakowsky and collaborators.

We have not made so detailed a calculation of the possible limits of error in the opposite direction. We notice, however, that the restricted internal rotation introduces less possible error in the direction of giving a lower value of $|\Delta H_{298^\circ}|$, and although the uncertainty becomes a little greater with the ethylene frequencies, the whole uncertainty in this direction is probably less than 600 cals. We therefore arrive at the figure $-\Delta H_{298^\circ} = 31{,}050 \pm 600$ cals.

The most serious assumption in the whole calculation is that which concerns the restricted rotator. We have therefore examined the effect of a still larger restricting potential (which is highly improbable). If we assume the maximum potential difference to be 1050 cals. instead of 525, then the specific-heat measurements of Eucken and Parts cannot be fitted with any reasonable choice of the uncertain frequencies—any reasonable choice gives a slower rise of the specific heat with temperature than was observed. But even the assumption of 1050 cals. would not suffice to give a value of $|\Delta H_{298^\circ}|$ in agreement with that found by Kistiakowsky and collaborators. Still higher restrictions are correspondingly in greater disagreement with the specific-heat measurements, with this exception: restricting potentials higher than about 3000 cals. would again lead to a possibility of reproducing the measured specific-heat curve in the range of the measurements of Eucken and Parts. We should now have a slow " twisting " frequency of about 300 cm.$^{-1}$ in place of the internal rotation. It can be seen, by utilising the calculations carried out by Frost (*loc. cit.*), that such a " twisting " frequency would also give agreement with the calorimetric determination of Kistiakowsky and collaborators.*

The only *experimental* evidence which directly contradicts this assumption of a potential hill of 3000 cals. or more is the work of Eucken and Weigert * on the specific-heat curve of ethane at low temperatures. The " twisting " frequency, if it existed, would not appear in the infra-red or Raman spectra except possibly in combination- or over-tones.

Although we find as *possible* limits of error in our calculation of ΔH_{298° ± 600 cals., we think that the probable limits are about ± 300 cals.

SUMMARY.

From the experimentally known equilibrium constant of the reaction $C_2H_4 + H_2 = C_2H_6$, the heat of reaction at absolute zero is calculated by means of the most probable values of the molecular constants required for the partition functions of ethylene and ethane, Giauque's computation of the free energy of hydrogen being used.

The corresponding heat of reaction at constant pressure at 298° Abs. is 31,050 cals., with a probable error of ± 300 cals. This is in agreement with the calorimetric determination by von Wartenberg and Krause, but differs by 1525 cals. from that obtained in the recent and much more extensive measurements by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, *viz.*, 32,575 ± 50 cals.

A detailed discussion is given of the limits of possible error in the statistical-mechanical calculation of the reaction heat, arising from : (1) error in the equilibrium measurements; (2) error in the moments of inertia of ethylene and ethane; (3) error in the vibration frequencies of ethylene; (4) uncertainty in the magnitude of the potential restricting free rotation of the methyl groups in ethane; (5) uncertainty in the vibration frequencies of ethane.

It is concluded that the maximum uncertainty in the statistical-mechanical calculation is ± 600 cals. in the heat of reaction at ordinary temperatures.

THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON.

[*Received, April 16th,* 1935.]