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Thermodynamic Properties of Gaseous 1,3-Butadiene and the Normal Butenes above 25°C

Equilibria in the System 1,3-Butadiene, *n*-Butenes, and *n*-Butane*

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Tables of the thermodynamic functions C_p° , H° , S° , and F° are given for 1,3-butadiene and the normal butenes for temperatures from 298.16°K to 1500°K for the substances in the ideal gas states at one atmosphere pressure. These have been prepared using reliable spectroscopic and molecular data, together with calorimetric entropies, gaseous specific heats, and heats of formation. Equilibrium constants are given for reactions in the system 1,3-butadiene, *n*-butenes, and *n*-butane. Available experimental data are compared with the calculations. The calorimetric data for 1,3-butadiene furnish strong evidence for the existence of two geometric (*cis-trans*) isomeric forms of 1,3-butadiene in appreciable concentrations at room temperatures. The two forms differ in energy by 2.3 kcal. mole⁻¹, and are separated by a C—C rotational barrier 2.6 kcal. mole⁻¹ above the lowest energy level of the *cis*, or higher, energy form.

I. INTRODUCTION

IN various earlier papers¹⁻⁴ results of measurements of thermodynamic properties of *n*-butane, *cis*-2-butene, 1-butene, and 1,3-butadiene as determined at The Pennsylvania State College and the National Bureau of Standards have been published. For *trans*-2-butene the entropy has been determined calorimetrically by Guttman and Pitzer⁵ at the University of California. In the present paper are presented tables of thermo-

dynamic properties of 1,3-butadiene and the three normal butenes in the ideal gas state based on spectroscopic data and accepted structural constants of the molecules, and such experimental values of entropy and heat capacity as are available. Tables of equilibrium constants for the system 1,3-butadiene, *n*-butenes, and *n*-butane are included together with experimental equilibrium data where available.

Values of the physical constants used in the calculations are:

$$\begin{aligned} R &= 1.98714 \text{ cal. mole}^{-1} \text{ deg.}^{-1}, \\ c_2 &= hc/k = 1.4384 \text{ cm deg.}, \\ N_0 &= 6.0228 \times 10^{23} \text{ mole}^{-1}, \\ \text{Atomic weight of hydrogen} &= 1.0080, \\ \text{Atomic weight of carbon} &= 12.01. \end{aligned}$$

The calorie used is the artificial calorie defined by 1 calorie = 4.1833 international joules.

II. HEATS OF FORMATION AT 0°K

The heats of formation of 1,3-butadiene and the normal butenes have been obtained from the heat of formation of *n*-butane and the heats of hydrogenation of 1,3-butadiene and the butenes to *n*-butane.

The heat of formation of *n*-butane in the ideal gas state at 0°K, that is E_0° , was obtained

* This paper is a revision of a report "The heat content and free energy of butadiene 1,3 and isoprene above 25°C. Equilibria in the dehydrogenation of *n*-butane and *n*-butenes to butadiene-1,3" by John G. Aston and George Szasz, Pennsylvania State College and F. G. Brickwedde, National Bureau of Standards. Submitted to the Office of the Rubber Director, July 23, 1943.

¹ J. G. Aston and G. H. Messerly, "The heat capacity and entropy, heats of fusion and vaporization, and the vapor pressure of *n*-butane," J. Am. Chem. Soc. **62**, 1917 (1940).

² R. B. Scott, W. Julian Ferguson, and F. G. Brickwedde, "Thermodynamic properties of *cis*-2-butene from 15° to 1500°K," J. Research Nat. Bur. Stand. **33**, 1 (1944).

³ J. G. Aston, H. L. Fink, A. B. Bestull, E. L. Pace, and G. J. Szasz, "The heat capacity and entropy, heats of fusion and vaporization and the vapor pressure of butene-1. The zero point entropy of the glass. The entropy of the gas from molecular data," J. Am. Chem. Soc. (in press).

⁴ R. B. Scott, R. D. Rands, Jr., C. H. Meyers, F. G. Brickwedde, and N. Bekkedahl, "Thermodynamic properties of 1,3-butadiene in the solid, liquid, and vapor states," J. Research Nat. Bur. Stand. **35**, 39 (1945).

⁵ L. Guttman and K. S. Pitzer, "*Trans*-2-butene. The heat capacity, heats of fusion and vaporization, and vapor pressure. The entropy and barrier to internal rotation," J. Am. Chem. Soc. **67**, 324 (1945).

by combining enthalpy differences for *n*-butane,⁶ C (graphite),⁷ and H₂,⁷ with the value -29812 cal. mole⁻¹ for the heat of formation of *n*-butane from its elements at 298.16°K as given by Prosen and Rossini.⁸

Values of E_0^0 for 1,3-butadiene and the butenes were calculated using: (1) the enthalpy of *n*-butane at 355°K given by the use of Pitzer's tables for ($H^0 - E_0^0$) for *n*-butane⁶ with the E_0^0 evaluated as previously described, (2) values for heats of hydrogenation at 355°K determined by Kistiakowsky, Ruhoff, Smith, and Vaughan^{9,10} corrected to the new atomic weight of carbon, (3) enthalpy differences of 1,3-butadiene and the butenes from the tables of the present paper, and (4) the enthalpy of H₂ from reference 7.

III. *n*-BUTANE

In view of the greater complexity of the *n*-butane spectrum compared with the spectra of the other C₄ hydrocarbons and the resulting greater uncertainty of its interpretation, Pitzer's 1944 tables⁶ of thermodynamic functions of *n*-butane were adopted since they are in agreement with the calorimetric data on S^0 and C_p^0 . We have used these tables unchanged except for values for 600°K which seemed in doubt on the basis of other table values, and have interpolated where necessary. A portion of his table values together with interpolated values is given in Table I.†

⁶ K. S. Pitzer, "Thermodynamics of gaseous paraffins. Specific heat and related properties," Ind. Eng. Chem. **36**, 829 (1944).

⁷ H. W. Woolley, M. Moskow, F. G. Brickwedde, and J. G. Aston, "Thermodynamics of synthetic rubber and related substances. VI. Equilibrium constants of some reactions involved in the production of 1,3-butadiene," Report to the Office of the Rubber Director, March 24, 1944. To be published as a paper.

⁸ E. J. Prosen and F. D. Rossini, "Heats of combustion and formation of the paraffin hydrocarbons at 25°C," J. Research Nat. Bur. Stand. **34**, 263 (1945).

⁹ G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, "Heats of organic reactions. IV. Hydrogenation of some dienes and of benzene," J. Am. Chem. Soc. **58**, 146 (1936).

¹⁰ G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, "Heats of organic reactions. II. Hydrogenation of some simpler olefinic hydrocarbons," J. Am. Chem. Soc. **57**, 876 (1935).

† In the tables of this paper the following conventions have been adopted: For enthalpy, H^0 , and for free energy, F^0 , the quantities are given as values above assumed zeros for the elements in their standard states at 0°K. ΔH^0 , ΔF^0 , and K are, respectively, the enthalpy of formation, the free energy of formation, and the equilibrium constant of formation of the compound from the elements in their standard states at the temperature T .

TABLE I. Free energy and related quantities of *n*-butane in the ideal gas state at 1 atmosphere pressure. ΔF^0 and K are the free-energy change and equilibrium constant, respectively, for the reaction forming *n*-butane from its elements in their standard states at $T^\circ\text{K}$ ($E_0^0 = -23340$ cal. mole⁻¹).

T °K	$-\left(\frac{F^0 - E_0^0}{T}\right)$ cal. deg. ⁻¹ mole ⁻¹	$-F^0$ cal. mole ⁻¹	ΔF^0 cal. mole ⁻¹	$\log_{10} K$ $-\Delta F^0/RT$ 2.3026
298.16	58.51	40780	-3750	2.747
300.00	58.61	40920	-3590	2.613
400	63.49	48730	+5440	-2.971
500	67.93	57300	14880	-6.503
600	72.06	66570	24590	-8.957
700	75.97	76510	34490	-10.768
800	79.70	87100	44510	-12.160
900	83.28	98290	54590	-13.257
1000	86.72	110060	64720	-14.144
1100	90.02	122360	74870	-14.876
1200	93.19	135160	85060	-15.491
1300	96.24	148450	95240	-16.012
1400	99.18	162190	105430	-16.459
1500	102.03	176380	115620	-16.846

IV. 1,3-BUTADIENE

Bradacs and Kahovec¹¹ investigated the Raman spectrum of 1,3-butadiene and concluded that the structure of this molecule at room temperature is *trans* with no appreciable concentration of a *cis* modification. This conclusion was based on a consideration of the correspondence between the butadiene spectra and the Raman and infra-red activities of the normal modes of vibration characteristic of a *trans* molecule, including polarizations of Raman lines. Earlier, Schomaker and Pauling¹² stated on the basis of the electron diffraction pattern of butadiene that the configuration is essentially coplanar and *trans* although they also stated that "the electron diffraction data are not incompatible with a mixture of *cis* and (predominantly) *trans* molecules. . . ." Price and Walsh¹³ did not find evidence of a second form in ultraviolet absorption and concluded that butadiene seemed to be mainly *trans*. Mulliken¹⁴

¹¹ K. Bradacs and L. Kahovec, "Studies in the Raman-effect. Communication 121: Butadiene, homogeneous and in solution," Zeits. f. physik. Chemie **B48**, 63 (1940).

¹² V. Schomaker and L. Pauling, "The electron diffraction investigation of the structure of benzene, pyridine, pyrazine, butadiene-1,3, cyclopentadiene, furan, pyrrole, and thiophene," J. Am. Chem. Soc. **61**, 1769 (1939).

¹³ W. C. Price and A. D. Walsh, "The absorption spectra of conjugated dienes in the vacuum ultraviolet," Proc. Roy. Soc. **A174**, 220 (1940).

¹⁴ R. S. Mulliken, "Structure and ultraviolet spectra of ethylene, butadiene, and their alkyl derivatives," Rev. Mod. Phys. **14**, 265 (1942).

indicated on the basis of quantum-mechanical calculations that the *cis* and *trans* varieties should differ by about 2500 calories per mole and that the *trans* variety should be the more stable, but he also expressed a doubt as to the reliability of the estimate of the energy difference. Rasmussen, Tunnicliff, and Brattain¹⁵ have claimed that the *cis* variety has the lower energy and predominates at dry ice temperatures but that at room temperature the *trans* variety predominates, basing their view on the existence of some coincidences of frequencies in the Raman and infra-red spectra and on a rapid change of the ultraviolet absorption coefficient with temperature.

It seems unlikely, however, that the frequency distribution would be so different for *cis* and *trans* forms of butadiene as to cause the relative abundance of the two forms to be overwhelmingly reversed in so limited a range of temperature. On the contrary, it would seem probable that many frequencies of the *cis* variety would be of about the same value as the corresponding frequencies of the *trans* variety.

It may also be pointed out that changes of absorption with temperature near the limit of a band are not unusual in substances which have only a single form and hence do not necessarily indicate a rapid change of equilibrium proportions of *cis* and *trans* butadiene. From these considerations it is concluded that the observations of Rasmussen, Tunnicliff, and Brattain do not show that the *cis* variety is the lower energy form. The thermodynamic measurements, including the entropy determined by Scott, Rands, Meyers, Brickwedde, and Bekkedahl⁴ and the gaseous specific heats determined by Aston, Moessen, Hardy, and Szasz,¹⁶ Templeton and Davies with Felsing,¹⁷ and Scott and Mellors,¹⁸ furnish conclusive evidence for the existence of a second variety of 1,3-butadiene

having an energy of the order of 2000 cal. mole⁻¹ higher than the more stable form, as it is impossible to fit the measured thermodynamic properties on the basis of any reasonable frequency assignment for a single variety. A paper failing to consider the *cis-trans* equilibrium has recently been published by Zeise,¹⁹ but the values for the thermodynamic properties listed therein are unsatisfactory. In the present paper the *trans* has been adopted as the more stable form since there is more evidence for this choice than against it.

In calculating the thermodynamic functions for butadiene, the *cis* and *trans* varieties are treated as two chemical compounds in equilibrium with each other. The product of the principal moments of inertia for over-all rotation, the reduced moment of inertia for internal rotation, and the effective distribution of frequencies other than the single bond torsion were taken the same for the *cis* as for the *trans* form. When this is done the equilibrium between *cis* and *trans* varieties is governed solely by the potential energy function assumed to form the barrier for the two varieties.

Contributions to the thermodynamic functions coming from internal rotation due to the single bond torsion were calculated for each of the two varieties using the methods and tables of Pitzer and Gwinn.²⁰ For each variety the quantity $Q_f = 2.7934 (10^{38} I_{\text{red}} T)^{1/2} / n$ was calculated with $1/n$ equal to that fraction of a complete revolution of internal rotation to be ascribed to the variety in question. For the lower energy form the torsional free energy function is obtained from Pitzer's table of $(F^0 - F_f^0)/T$ using the formula

$$\frac{(F^0_{\text{trans}} - E^0_{0\text{trans}})_{\text{tors}}}{T} = -\frac{F^0}{T} = R \ln Q_f - \frac{(F^0 - F_f^0)}{T},$$

where the subscript *f* refers to hypothetical free

¹⁵ R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, "The configuration of 1,3 butadiene," J. Chem. Phys. 11, 432 (1943).

¹⁶ J. G. Aston, G. W. Moessen, H. C. Hardy, and G. J. Szasz, "The heat capacity of gaseous butadiene-1,3," J. Chem. Phys. 12, 458 (1944).

¹⁷ D. H. Templeton and D. D. Davies with W. A. Felsing, "The heat capacity of gaseous 1,3-butadiene from 0 to 100°," J. Am. Chem. Soc. 66, 2033 (1944).

¹⁸ R. B. Scott and J. W. Mellors, "Specific heats of gaseous 1,3-butadiene, isobutene, styrene, and ethylbenzene," J. Research Nat. Bur. Stand. 34, 243 (1945).

¹⁹ H. Zeise, "The thermodynamic functions of gaseous butadiene and the equilibrium constant for the decomposition of butylene into butadiene and hydrogen," Zeits. f. Elektrochemie 50, 113 (1944).

²⁰ K. S. Pitzer and W. D. Gwinn, "Energy levels and thermodynamic functions for molecules with internal rotation. I. Rigid frame with attached tops," J. Chem. Phys. 10, 428 (1942).

rotation. For the higher energy form a similar quantity can be calculated

$$\frac{(F^0_{cis} - E^0_{cis})_{tors}}{T} = -\frac{F^0}{T} = R \ln Q_f - \frac{(F^0 - F_f^0)}{T},$$

using constants appropriate to the *cis* variety. To treat the equilibrium between the two forms, the quantity

$$\frac{(F^0_{cis} - E^0_{trans})_{tors}}{T} = R \ln Q_f - \frac{(F^0 - F_f^0)}{T} - \frac{\Delta E^0_0}{T}$$

is to be evaluated, where $\Delta E^0_0 = E^0_{cis} - E^0_{trans}$,

$$\begin{aligned} \frac{H^0 - E^0}{T} &= X_{cis} \left[\frac{H^0_{cis} - E^0_{cis}}{T} + \frac{E^0_{cis} - E^0_{trans}}{T} \right] + X_{trans} \left[\frac{H^0_{trans} - E^0_{trans}}{T} \right], \\ -\left(\frac{F^0 - E^0_0}{T} \right) &= X_{cis} \left[-\left(\frac{F^0_{cis} - E^0_{cis}}{T} \right) - \frac{E^0_{cis} - E^0_{trans}}{T} \right] + X_{trans} \left[-\left(\frac{F^0_{trans} - E^0_{trans}}{T} \right) \right] \\ &\quad - R[X_{cis} \ln X_{cis} + X_{trans} \ln X_{trans}], \\ S^0 &= X_{cis} S^0_{cis} + X_{trans} S^0_{trans} - R[X_{cis} \ln X_{cis} + X_{trans} \ln X_{trans}], \\ C_p^0 &= X_{cis} C_p^0_{cis} + X_{trans} C_p^0_{trans} + \frac{X_{cis} X_{trans}}{R} \left[\frac{H^0_{cis} - E^0_{cis}}{T} + \frac{E^0_{cis} - E^0_{trans}}{T} - \frac{H^0_{trans} - E^0_{trans}}{T} \right]^2. \end{aligned}$$

The spectroscopic data for 1,3-butadiene include the Raman spectra of Bradacs and Kahovec,¹¹ and of Dadiou and Kohlrausch,²¹ and the infra-red spectra of Bartholomé and Karweil,²² and of the American Petroleum Institute.²³ Data in a more recent paper by Yao²⁴ do not lead to any change in the assignment. The fundamental frequencies, in cm^{-1} , assigned to the

the estimated difference in energies of the two forms in their lowest quantum levels. The equilibrium constant for the formation of the *cis* form from the *trans* form is given by

$$K = X_{cis}/X_{trans},$$

with

$$R \ln K = -\frac{\Delta F^0}{T} = -\frac{(F^0_{cis} - E^0_{trans})_{tors}}{T} - \left[-\frac{(F^0_{trans} - E^0_{trans})_{tors}}{T} \right],$$

where the *X*'s refer to mole fractions. The thermodynamic functions for the mixture are obtained from the complete functions for the two varieties using the formulas

normal modes of vibration of the *trans* variety of the butadiene molecule (point group C_{2h}) are as follows, where the symbols have the same significance as in Kohlrausch's book.²⁵ The symbols (*p*) and (*dp*) denote polarized and unpolarized Raman lines while (*i.r.*) denotes an infra-red band. The values given in parentheses were not observed spectroscopically but were selected on other considerations.

Carbon skeleton frequencies

$$A_g: \omega_1, 1635 (p); \omega_2, 1200 (p); \omega_3, 513 (p) \\ B_u: \omega_4, 1602 (i.r.); \omega_5, (326).$$

$\gamma(\text{C-H})$ rocking frequencies

$$A_u: 520 (i.r.), 910 (i.r.), 1014 (i.r.) \\ B_g: (667), 899 (dp), 914 (dp).$$

²¹ A. Dadiou and K. W. F. Kohlrausch, "Raman effect and constitutional problems," Ber. d. d. chem. Ges. **63**, 1657 (1930).

²² E. Bartholomé and J. Karweil, "The infra-red spectrum and the fundamental vibration bands of the hydrocarbons biacetylene, butadiene and vinylacetylene," Zeits. f. physik. Chemie **B35**, 442 (1937).

²³ American Petroleum Institute, "Infra-red absorption spectrograms," issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

²⁴ Y. T. Yao, "Absorption bands in the spectrum of butadiene," paper presented at the Columbus meeting of the American Physical Society, June 15, 1945.

²⁵ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin, 1931-1937), Supplement, pp. 44 and 69.

$\delta(\text{C}-\text{H})$ bending frequencies

A_g : 1276 (*p*), 1303 (*p*), 1437 (*p*)

B_u : 1282 (*i.r.*), 1385 (*i.r.*), 1490 (*i.r.*).

$\nu(\text{C}-\text{H})$ stretching frequencies

A_g : 3000, 3088, 3000

B_u : three 3000.

Except for several frequencies which are here mentioned explicitly, the assignment given is that of Bradacs and Kahovec.¹¹ Values for the torsional frequencies associated with the double bonds have been selected on the basis of the corresponding value for ethylene. The estimates were 587 cm^{-1} for the A_u mode and 667 cm^{-1} for the B_g mode. The 587 cm^{-1} was shifted to the observed 520 cm^{-1} and the calculated value 667 cm^{-1} has been retained unchanged. Force constant calculations were also made for the skeletal deformation vibrations. They indicated that for $\omega_3 = 513 \text{ cm}^{-1}$, ω_5 would be expected to be about 345 cm^{-1} . This value was lowered to 326 cm^{-1} in fitting the experimental thermodynamic data. Some of the frequencies used for the *trans* molecule may belong to the *cis* variety. A few observed frequencies were not used but it is not difficult to account for them in a way that seems plausible. The weak infra-red line at 665 cm^{-1} is presumed to belong to the *cis* form. The very weak Raman line at 1782 cm^{-1} may be the overtone of the 899 cm^{-1} fundamental and the weak Raman line at 1025 cm^{-1} is regarded as the overtone of ω_3 , 513 cm^{-1} . A weak Raman line occurring at 340 cm^{-1} is taken to be caused by an overtone of a frequency at 170 cm^{-1} for the single bond torsion for the *trans* form. Calculations of the type recommended by Lord²⁶ using low temperature specific heat data for crystalline butadiene favored the use of a frequency of this general magnitude for the lowest molecular frequency. Preliminary adjustments to fit S^0 and C_p^0 at 300°K also indicated essentially this value.

The values used for bond lengths and angles were selected on the basis of the work and recommendations of Schomaker and Pauling¹² and of Galloway and Barker;²⁷ C-H, 1.09A;

C-C, 1.46A; $\angle \text{C}-\text{C}=\text{C}$, 124°; $\angle \text{H}-\text{C}=\text{C}$, 115°; $\angle \text{H}-\text{C}-\text{H}$, 120°. These lead to the value $ABC = 0.8186 \times 10^{-114} \text{ g}^3 \text{ cm}^6$ for the product of the principal moments of inertia and to $10.282 \times 10^{-40} \text{ g cm}^2$ for the reduced moment of inertia for internal rotation for the *trans* variety of butadiene. Thus the expressions for the entropy, free energy function, and heat capacity of translational and molecular rotational motions in cal. $\text{deg}^{-1} \text{ mole}^{-1}$ are

$$S^0_{t+r} = 18.302_2 \log_{10} T + 14.835, \quad (1)$$

$$\begin{aligned} -\left(\frac{F^0 - E_0^0}{T}\right)_{t+r} &= S^0_{t+r} - \left(\frac{H^0 - E_0^0}{T}\right)_{t+r} \\ &= S^0_{t+r} - 4R \\ &= 18.302_2 \log_{10} T + 6.886, \quad (2) \end{aligned}$$

$$C^0_{p, t+r} = 7.949. \quad (3)$$

The addition to the above Eqs. (1) and (3) of the intra-molecular vibrational contributions apart from the undetermined ω_5 and the single C-C bond torsion yields values which, when subtracted from the calorimetric values of S^0 and C_p^0 , are the entropy and specific heat contributions of ω_5 and the torsional oscillation of the two vinyl groups about the middle C-C bond. A simultaneous fit of entropy, specific heat, and change of specific heat with temperature was obtained, working with ω_5 and the parameters V_0 , *trans*, V_0 , *cis*, and

$$1/n_{cis} = 1 - (1/n_{trans})$$

of barriers for internal rotation of the *trans* and *cis* forms about the C-C bond where the barriers are given by the equation

$$V = 0.5 V_0 [1 - \cos n\theta].$$

The resulting shape of the barrier is shown as the continuous curve in Fig. 1. The constants found were $1/n = 0.406$ and $V_0 = 5000 \text{ cal. mole}^{-1}$ for the *trans* barrier and $1/n = 0.594$ and $V_0 = 2575 \text{ cal. mole}^{-1}$ for the *cis* barrier while ω_5 was adjusted to 326 cm^{-1} . Thus, 40.6 percent of the angle of rotation about the central C-C bond was assigned to the *trans* form and 59.4 percent of the angle to the *cis* form. When allowance is made for zero point energy, the lowest quantum level of the *cis* form is approximately 2300 cal. mole^{-1} higher than the lowest quantum level of the *trans* form. While significance is attached

²⁶ R. C. Lord, Jr., "The heat capacities of molecular lattices. I. Introduction," J. Chem. Phys. 9, 693 (1941).

²⁷ W. S. Galloway and E. F. Barker, "The infra-red absorption spectra of ethylene and tetra-deutero-ethylene under high resolution," J. Chem. Phys. 10, 88 (1942).

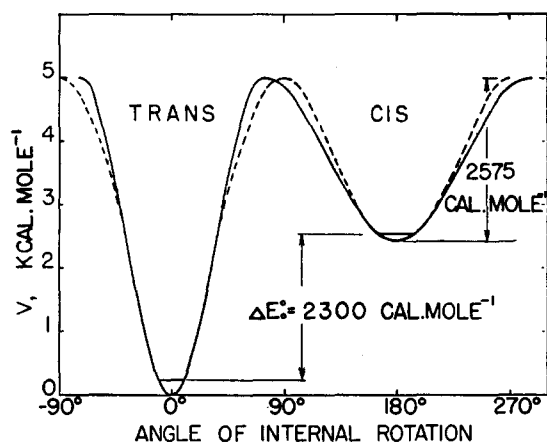


FIG. 1. Potential energy as a function of the angle of torsion about the central C—C bond in 1,3-butadiene. The continuous curve represents the barriers used in the calculations of Tables II and III:

$$V_{trans} = 2.500[1 - \cos(\theta/0.406)] \text{ in kcal. mole}^{-1}$$

and

$$V_{cis} = 2.425 + 1.288[1 - \cos([\theta - \pi]/0.594)] \text{ in kcal. mole}^{-1}.$$

The dashed curve represents a modified potential energy function giving the same thermodynamic properties.

to the general features of the *cis-trans* barrier as given here, it must be pointed out that the exact details are quite uncertain. Thus, in Fig. 1, the dashed curve has been so constructed as to provide essentially the same over-all distribution of levels with regard to energy (and therefore the same thermodynamic functions) as occurs for the continuous curve. For the dashed curve, 50 percent of the angle of rotation belongs to the *trans* form and 50 percent to the *cis* form, as might be expected from the theory of bond conjugation. With the dashed curve, the concentration of the *cis* form would be slightly less than with the continuous curve.

Calculated and experimental values of the specific heat of 1,3-butadiene in the ideal gas state are plotted in Fig. 2. In Tables II and III are given the calculated thermodynamic functions of 1,3-butadiene and the mole fraction of its *cis* form.

V. TRANS-2-BUTENE

The Raman and infra-red spectra of *trans*-2-butene have been photographed by Gershinowitz and Wilson.²⁸

²⁸ H. Gershinowitz and E. B. Wilson, Jr., "Infra-red and Raman spectra of polyatomic molecules. II. *Cis*- and *trans*-butene-2," J. Chem. Phys. 6, 247 (1938).

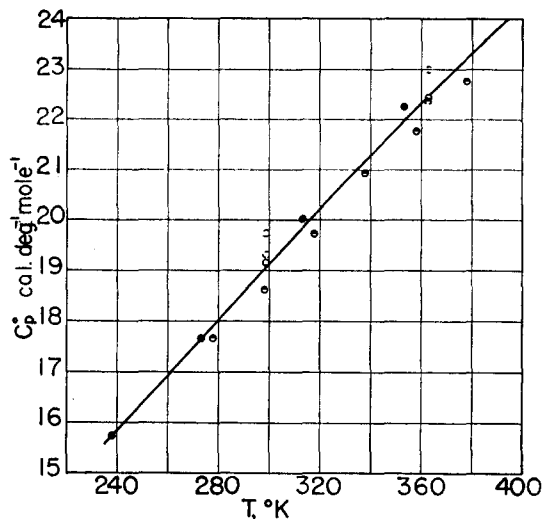


FIG. 2. Specific heat of gaseous 1,3-butadiene in the ideal gas state.

● Scott and Mellors

● Templeton and Davies with Felsing

○, ○, ○ Aston, Moessen, Hardy and Szasz, data variously corrected to zero pressure.

The curve represents the calculated values of this paper.

This molecule, like butadiene, belongs to the symmetry class C_{2h} , which allows no coincidences between the Raman and infra-red spectra. There are (excluding internal rotation) twenty-eight modes of vibration to which frequencies must be assigned. With the same notation used for butadiene, the assignment adopted was as follows:

Carbon skeleton frequencies:

$$A_g: \omega_1, 1681 (p); \omega_2, 870 (p); \omega_3, 507 (p)$$

$$B_u: \omega_4, 978 (i.r.); \omega_5, (313)(i.r.); \omega_6, (270).$$

Frequencies due to CH groups:

$$A_g: \nu_1, 2739 (p); \delta_1, 1309 (p)$$

$$A_u: \gamma_1, 1080 (i.r.)$$

$$B_g: \gamma_2, 1043 (dp)$$

$$B_u: \nu_2, 2427 (i.r.); \delta_2, 1326 (i.r.).$$

Frequencies due to CH_3 groups:

$$A_g: \nu_3(\pi), 2867 (p); \delta_3(\pi), 1309 (p); \nu_4(\sigma), 2965 (p); \delta_4(\sigma), 1309 (p); \gamma_3, 870 (p)$$

$$A_u: \nu_5(\sigma), 2976 (i.r.); \delta_5(\sigma), 1466 (i.r.); \gamma_4, 1072 (i.r.); \text{internal rotation}$$

$$B_g: \nu_6(\sigma), 2926 (dp); \delta_6(\sigma), 1455 (dp); \gamma_5, 746 (dp); \text{internal rotation}$$

$$B_u: \nu_7(\pi), 2976 (i.r.); \delta_7(\pi), 1560 (i.r.); \nu_8(\dot{\sigma}), 2976 (i.r.); \delta_8(\sigma), 1488 (i.r.); \gamma_6, 1214 (i.r.).$$

The frequency ω_6 was not observed but filled in by analogy with other molecules. The frequency ω_5 was too low to be observed in the infra-red and the value 313 cm^{-1} obtained by the normal coordinate treatment of O. Burkard²⁹ was chosen. The symbols π and σ are used to denote vibrations in which both methyl groups vibrate essentially as they do in methyl chloride vibrations of the π and σ type, respectively. These symbols in addition to the symmetry class uniquely specify the types of vibration. The symbols (p) and (dp) denote polarized and unpolarized Raman lines while $(i.r.)$ denotes an infra-red line (or band).

The distances and angles used were: C—C, 1.54Å; C—H, 1.09Å; C=C, 1.36Å; and $\angle\text{C—C—H}$, $109^\circ 28'$. Thus the product ABC of the principal moments of inertia is $1.449 \times 10^{-114}\text{ g}^3\text{ cm}^6$, and the reduced moment of inertia I_{red} of a methyl group is $5.0 \times 10^{-40}\text{ g cm}^2$.

The entropy and free energy of the translation and external rotation of the molecule together with free internal rotations of the methyl groups are

$$S^0_{t+r+fr} = 22.875 \log T + 11.239, \quad (4)$$

$$-\left(\frac{F^0 - E_0^0}{T}\right)_{t+r+fr} = 22.875 \log T + 1.305. \quad (5)$$

TABLE II. Heat capacity at constant pressure, heat content and related quantities of 1,3-butadiene in the ideal gas state, and the mole fraction X_{cis} of the *cis* form of 1,3-butadiene in the mixture of *cis* and *trans* forms. ΔH^0 is the enthalpy of formation of 1,3-butadiene from its elements in their standard states at the temperature T ($E_0^0 = 30200\text{ cal.mole}^{-1}$).

T	X_{cis}	$\frac{H^0 - E_0^0}{T}$	H^0	ΔH^0	C_p^0
°K		cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹
298.16	0.04	12.16	33830	26750	19.01
300.00	.04	12.20	33860	26730	19.11
400	.09	14.59	36040	25830	24.29
500	.16	16.97	38690	25120	28.52
600	.22	19.18	41710	24540	31.84
700	.27	21.19	45040	24080	34.55
800	.32	23.01	48610	23710	36.84
900	.35	24.66	52390	23420	38.81
1000	.38	26.16	56360	23210	40.52
1100	.40	27.54	60490	23060	42.02
1200	.42	28.80	64760	22980	43.32
1300	.44	29.96	69150	22940	44.47
1400	.45	31.03	73650	22950	45.47
1500	.46	32.02	78240	22980	46.34

²⁹ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin, 1938), Supplement, p. 10.

Adding to S^0_{t+r+fr} the contributions made by the internal vibrations, an entropy value was obtained which was used with Pitzer's experimental value,⁵ $69.12\text{ cal. deg.}^{-1}\text{ mole}^{-1}$, of the entropy at 274.1°K to calculate the potential restricting rotation of the methyl groups. The value found is $1900\text{ cal. mole}^{-1}$.

The calculated heat capacities are compared in Table IV with the calorimetric data of Kistiakowsky and Rice.³⁰

Values of the thermodynamic functions for *trans*-2-butene are summarized in Tables V and VI.

VI. CIS-2-BUTENE

The thermodynamic functions of *cis*-2-butene are from reference 2 using a new value for E_0^0 and are based on spectroscopic, molecular, and calorimetric data discussed in that publication. The change of value for E_0^0 is caused by changes in the values used for the heat of formation and thermodynamic functions of *n*-butane.

Values of thermodynamic functions of *cis*-2-butene are given in Tables VII and VIII.

VII. 1-BUTENE

The entropy of 1-butene in the standard ideal gas state at the normal boiling point, 266.91°K ,

TABLE III. Entropy, free energy, and related quantities of 1,3-butadiene in the ideal gas state at 1 atmosphere pressure. ΔF^0 and K are the free energy change and equilibrium constant, respectively, for the reaction forming 1,3-butadiene from its elements in their standard states at $T^\circ\text{K}$ ($E_0^0 = 30200\text{ cal. mole}^{-1}$).

T	$-\left(\frac{F^0 - E_0^0}{T}\right)$	S^0	$-F^0$	ΔF^0	$\log_{10} K$
°K	cal. deg. ⁻¹ mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	$-\Delta F^0/RT$ 2.3026
298.16	54.46	66.62	-13960	36430	-26.707
300.00	54.44	66.74	-13840	36490	-26.587
400	58.38	72.97	-6850	39890	-21.793
500	61.89	78.86	+740	43490	-19.009
600	65.18	84.36	8920	47210	-17.198
700	68.29	89.48	17600	51040	-15.934
800	71.24	94.25	26790	54920	-15.003
900	74.05	98.71	36440	58830	-14.287
1000	76.72	102.88	46520	62780	-13.721
1100	79.28	106.82	57010	66740	-13.260
1200	81.73	110.53	67880	70720	-12.880
1300	84.09	114.05	79110	74690	-12.557
1400	86.35	117.38	90680	78670	-12.281
1500	88.52	120.54	102580	82660	-12.043

³⁰ G. B. Kistiakowsky and W. W. Rice, "Gaseous heat capacities. II," J. Chem. Phys. 8, 610 (1940).

TABLE IV. A comparison of the calculated and experimental values for the heat capacity of *trans*-2-butene in the ideal gas state.

T °K	C_p^0 (calc.)	C_p^0 (expt.)	
	cal. deg. ⁻¹ mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹ _a	cal. deg. ⁻¹ mole ⁻¹ _b
298.6	20.90	20.98	20.81
332.9	22.61	22.69	22.61
371.5	24.51	24.53	24.51

^a For the ideal gas state as reported by Kistiakowsky and Rice using Roper's equation of state (see reference 30).

^b For the ideal gas state using experimental data of Kistiakowsky and Rice and the equation of state for *cis*-2-butene (see reference 2).

has been determined calorimetrically³ as 70.87 ± 0.21 cal. deg.⁻¹ mole⁻¹. Preliminary values of the specific heat of gaseous 1-butene in the ideal gas state as determined by Scott and Wacker³¹ are 21.46 cal. deg.⁻¹ mole⁻¹ at 313.56°K and 24.18 cal. deg.⁻¹ mole⁻¹ at 363.26°K. With these data it is possible to evaluate the thermodynamic properties from the incomplete spectroscopic data with more certainty than originally obtained by Pitzer.³²

The symmetry class to which this molecule belongs depends on the relative position of the ethyl and vinyl groups. If all the atoms are coplanar it is $C_{1h} = C_s$, otherwise, it is C_1 . In either case, all lines should appear in the Raman spectrum and in the infra-red, but in the former, Raman lines caused by modes symmetrical with respect to the plane of symmetry would be polarized. Unfortunately, no polarization measurements have been reported for the Raman spectra so that this important clue concerning the form of the molecule is lacking.

The Raman and infra-red spectra indicate essentially only one form. A calculation of the barrier for the rotation of vinyl and ethyl groups with respect to each other based on hydrogen repulsions alone³ would indicate two non-planar stable configurations which are optical isomers lying on either side of the planar *trans* configuration. Each of these non-planar forms occupies about one third of a revolution. The

Raman spectrum does not indicate the presence of an appreciable concentration of a second or planar form.

The Raman spectrum of this compound has been studied by Kohlrausch and Stockmair,³³ while the infra-red data have been obtained from American Petroleum Institute Spectrograms.²³

From these results the following frequency assignment has been made:

	cm ⁻¹
C=C stretching	1636
C-C stretching	850 and 1068
CH ₃ internal angle change	1450(2), 1376(1)
skeleton angle change	320, 437
=CH ₂ internal angle change	1416
=CH ₂ torsion	623
CH wagging in plane	1293
CH wagging out of plane	908
CH ₃ wagging	972, 1019
-CH ₂ twisting	1257
CH ₂ wagging	(940), 1315
CH ₂ internal angle change	1450
=CH ₂ wagging	995, 1166
CH stretching	2950(8)

In making this assignment, the assignments made for propane by Pitzer³⁴ and for propylene

TABLE V. Heat capacity at constant pressure, heat content and related quantities of *trans*-2-butene in the ideal gas state. ΔH^0 is the enthalpy of formation of *trans*-2-butene from its elements in their standard states at the temperature T ($E_0^0 = 2520$ cal. mole⁻¹).

T °K	$\frac{H^0 - E_0^0}{T}$	H^0	ΔH^0	C_p^0
	cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹
298.16	14.03	6700	-2400	20.88
300.00	14.07	6740	-2420	20.97
400	16.40	9080	-3860	25.89
500	18.78	11910	-5090	30.57
600	21.11	15180	-6120	34.78
700	23.32	18850	-6950	38.48
800	25.42	22860	-7580	41.68
900	27.39	27170	-8050	44.47
1000	29.22	31740	-8380	46.89
1100	30.92	36540	-8580	48.99
1200	32.51	41530	-8680	50.80
1300	33.97	46690	-8690	52.36
1400	35.32	51970	-8660	53.71
1500	36.61	57430	-8530	54.89

³¹ R. B. Scott and P. F. Wacker, Nat. Bur. Stand. unpublished data.

³² K. S. Pitzer, "Thermodynamics of gaseous hydrocarbons: ethane, ethylene, propane, propylene, *n*-butane, isobutane, 1-butene, *cis*- and *trans*-2-butenes, isobutene, and neopentane (tetramethylmethane)," J. Chem. Phys. 5, 473 (1937).

³³ K. W. F. Kohlrausch and W. Stockmair, "Studies in the Raman effect. Communication 44. Raman effect and free rotation. III," Zeits. f. physik. Chemie B29, 292 (1935).

³⁴ K. S. Pitzer, "The molecular structure and thermodynamics of propane. The vibration frequencies, barrier to internal rotation, entropy, and heat capacity," J. Chem. Phys. 12, 310 (1944).

TABLE VI. Entropy, free energy, and related quantities of *trans*-2-butene in the ideal gas state at 1 atmosphere pressure. ΔF^0 and K are the free energy change and equilibrium constant, respectively, for the reaction forming *trans*-2-butene from its elements in their standard states at $T^\circ\text{K}$ ($E_0^0 = 2520 \text{ cal. mole}^{-1}$).

T	$-\left(\frac{F^0 - E_0^0}{T}\right)$	S^0	$-F^0$	ΔF^0	$\log_{10} K$
$^\circ\text{K}$	cal. deg. ⁻¹ mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	$-\Delta F^0/RT$ 2.3026
298.16	56.91	70.95	14450	15300	-11.217
300.00	57.00	71.07	14580	15410	-11.228
400	61.38	77.78	22030	21570	-11.784
500	65.29	84.07	30120	28080	-12.274
600	68.91	90.02	38830	34810	-12.681
700	72.33	95.65	48110	41710	-13.022
800	75.60	101.02	57960	48700	-13.304
900	78.69	106.08	68310	55770	-13.543
1000	81.68	110.90	79160	62880	-13.742
1100	84.54	115.47	90480	70010	-13.910
1200	87.30	119.81	102250	77160	-14.053
1300	89.96	123.94	114430	84310	-14.174
1400	92.54	127.87	127040	91440	-14.275
1500	95.01	131.62	140000	98620	-14.369

by Wilson and Wells³⁵ were considered. The 940 cm^{-1} frequency which has been used for a CH_2 wagging motion was not found in the 1-butene spectra but has been used to be consistent with the schematic frequency system for a CH_2 group as indicated by Pitzer. A 1-butene infra-red line at 1130 cm^{-1} was under consideration for this motion but it was found in only one of several infra-red investigations and, if not due to an impurity, may well have been a difference frequency, since $1450 - 320 = 1130$.

The bond lengths and angles used were: C—C, 1.54 Å; C=C, 1.36 Å; C—H, 1.09 Å; <C—C—C, $109^\circ 28'$; <C—C—H, $109^\circ 28'$. The average of the products of moments of inertia about principal axes of the planar and non-planar forms is then

$$ABC = 1.53 \times 10^{-114} \text{ g}^3 \text{ cm}^6.$$

The reduced moment (using axes through the centers of gravity of the groups parallel to the bond) for the mutual rotation of the ethyl and vinyl groups is

$$I_{\text{red}} = 13.37 \times 10^{-40} \text{ g cm}^2,$$

while that for the internal rotation of the methyl

³⁵ E. B. Wilson, Jr., and A. J. Wells, "Infra-red and Raman spectra of polyatomic molecules. XIV. Propylene," J. Chem. Phys. 9, 319 (1941).

TABLE VII. Heat capacity at constant pressure, heat content and related quantities of *cis*-2-butene in the ideal gas state. ΔH^0 is the enthalpy of formation of *cis*-2-butene from its elements in their standard states at the temperature T ($E_0^0 = 3710 \text{ cal. mole}^{-1}$).

T	$\frac{H^0 - E_0^0}{T}$	H^0	ΔH^0	C_p^0
$^\circ\text{K}$	cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹
298.16	13.50	7740	-1360	19.17
300.00	13.53	7770	-1400	19.27
400	15.63	9960	-2970	24.56
500	17.92	12670	-4330	29.57
600	20.24	15860	-5450	33.96
700	22.48	19450	-6340	37.74
800	24.60	23390	-7050	41.00
900	26.59	27640	-7580	43.83
1000	28.44	32150	-7970	46.28
1100	30.16	36890	-8230	48.41
1200	31.76	41820	-8390	50.25
1300	33.24	46930	-8450	51.85
1400	34.62	52180	-8450	53.23
1500	35.90	57560	-8400	54.44

TABLE VIII. Entropy, free energy, and related quantities of *cis*-2-butene in the ideal gas state at 1 atmosphere pressure. ΔF^0 and K are the free-energy change and equilibrium constant, respectively, for the reaction forming *cis*-2-butene from its elements in their standard states at $T^\circ\text{K}$ ($E_0^0 = 3710 \text{ cal. mole}^{-1}$).

T	$-\left(\frac{F^0 - E_0^0}{T}\right)$	S^0	$-F^0$	ΔF^0	$\log_{10} K$
$^\circ\text{K}$	cal. deg. ⁻¹ mole ⁻¹	cal. deg. ⁻¹ mole ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	$-\Delta F^0/RT$ 2.3026
298.16	58.32	71.82	13680	16070	-11.782
300.00	58.41	71.94	13810	16180	-11.787
400	62.59	78.22	21330	22270	-12.170
500	66.32	84.24	29450	28750	-12.567
600	69.79	90.03	38160	35480	-12.923
700	73.07	95.55	47440	42380	-13.231
800	76.21	100.81	57260	49400	-13.494
900	79.22	105.81	67590	56480	-13.716
1000	82.12	110.56	78410	63630	-13.906
1100	84.91	115.07	89690	70800	-14.066
1200	87.61	119.37	101420	77990	-14.204
1300	90.21	123.45	113560	85180	-14.320
1400	92.73	127.35	126110	92380	-14.421
1500	95.16	131.06	139030	99580	-14.509

group is

$$I_{\text{red}} = 5.0 \times 10^{-40} \text{ g cm}^2.$$

A potential of 2700 cal. mole^{-1} was assumed to hinder the internal rotation of the methyl group. The expression for the entropy of translation and total rotation (including free internal rotation) in $\text{cal. deg.}^{-1} \text{ mole}^{-1}$, is

$$S_{t+r+f \text{ int rot}} = 22.875 \log T + 15.048.$$

TABLE IX. A comparison of calculated and experimental specific heats and entropies for 1-butene in the standard ideal gas state.

T °K	C_p^0 (calc.) cal. deg. ⁻¹ mole ⁻¹	C_p^0 (expt.) cal. deg. ⁻¹ mole ⁻¹
313.56	21.52	21.46
363.26	24.17	24.18
T °K	S^0 (calc.) cal. deg. ⁻¹ mole ⁻¹	S^0 (expt.) cal. deg. ⁻¹ mole ⁻¹
200.00	65.88	66.24
230.00	68.18	68.49
266.91	70.87	70.87

At the normal boiling point (266.91°K) the experimental entropy of the ideal gas is 70.87 cal. deg.⁻¹ mole⁻¹. The vibrational entropy, calculated from the above spectrum, is 2.75 cal. deg.⁻¹ mole⁻¹ while the entropy due to translation and total rotation without correction for restriction is 70.55 cal. deg.⁻¹ mole⁻¹. The restricting correction for the methyl group rotation obtained from the tables of Pitzer and Gwinn²⁰ is 1.33 cal. deg.⁻¹ mole⁻¹. The correction for the restriction of the ethyl group rotation must thus be 1.10 cal. deg.⁻¹ mole⁻¹. A barrier of about 2000 cal. mole⁻¹ gives essentially this correction. In order also to fit the experimental gaseous specific heats, further adjustment of details of the barrier was required. A plot of the potential energy calculated on the basis of hydrogen repulsions³ suggests that in the region of the planar *trans* form there is so little change of energy with angle that this region may be considered as an energy plateau. This plateau-like region was taken as occupying 12 percent of a revolution with each of the two non-planar forms occupying 30 percent of a revolution and having potential energy valleys of 1970 cal. mole⁻¹. The calculation procedure for a mixture of different forms of molecule has been indicated in the discussion of the calculations for butadiene.

In the paper by Aston *et al.*³ the entropy is given not only for 266.91°K but also for 200°K and 230°K. As will be seen from Table IX, it is found that when the experimental specific heats at 313.56°K and 363.26°K and the entropy at 266.91°K are fitted, the agreement of the calorimetric and calculated entropies for 200°K and 230°K is not exact. From one standpoint it seemed preferable to fit the value reported for

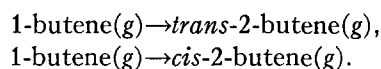
266.91°K since in this temperature region the reported thermal data satisfy the Clapeyron equation better than at the two lower temperatures.

Tables X and XI list the thermodynamic properties of 1-butene calculated as outlined in this section.

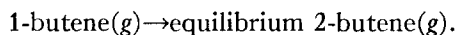
VIII. EQUILIBRIA

1. Equilibrium Constants for the Isomerization of 1-Butene(*g*) to 2-Butene(*g*)

From the data discussed in the preceding sections the equilibrium constants have been calculated for the reactions



The sum of the equilibrium constants for these two reactions is the equilibrium constant for the reaction



The results for the three reactions are summarized in Table XII.

In Fig. 3 the results for the reaction 1-butene \rightarrow equilibrium 2-butene are shown in comparison with experimental data determined by McCarthy and Turkevich,³⁶ Frey and Huppke,³⁷ Runge and

TABLE X. Specific heat at constant pressure, heat content and related quantities of 1-butene in the ideal gas state. ΔH^0 is the enthalpy of formation of 1-butene from its elements in their standard states at the temperature T ($E_0 = 5370$ cal. mole⁻¹).

T °K	$\frac{(H^0 - E_0^0)}{T}$ cal. deg. ⁻¹ mole ⁻¹	H^0 cal. mole ⁻¹	ΔH^0 cal. mole ⁻¹	C_p^0 cal. deg. ⁻¹ mole ⁻¹
298.16	13.60	9425	325	20.69
300.00	13.64	9460	300	20.79
400	16.09	11810	-1130	26.07
500	18.59	14660	-2340	30.90
600	20.99	17960	-3340	35.08
700	23.27	21660	-4130	38.68
800	25.39	25680	-4760	41.79
900	27.37	30000	-5220	44.50
1000	29.20	34570	-5550	46.85
1100	30.90	39360	-5760	48.90
1200	32.48	44350	-5860	50.68
1300	33.94	49490	-5890	52.22
1400	35.29	54780	-5850	53.57
1500	36.56	60210	-5750	54.74

³⁶ W. W. McCarthy and J. Turkevich, "Butene-1 and butene-2 equilibrium," J. Chem. Phys. 12, 405 (1944).

³⁷ F. E. Frey and W. F. Huppke, "Equilibrium dehydrogenation of ethane, propane, and the butenes," Ind. Eng. Chem. 25, 54 (1933).

Mueller-Conradi,³⁸ and Hurd and Goldsby³⁹ plotted as $\log_{10} K$ against a scale linear in $1/T$. The agreement of the calculated curve with the data of McCarthy and Turkevich, which appear more reliable than the other equilibrium data, would be improved appreciably if for 1-butene the calorimetric value of the entropy had been fitted at 200°K rather than at 266.91°K but it is thought that other uncertainties in both the experimental and calculated data are sufficient to account for the differences between observed and calculated equilibrium constants. Thus the fit of the experimental and calculated equilibrium constants could be improved by small adjustments in the *cis*- and *trans*-2-butene data. Comparisons of calculated equilibrium constants with reliable experimental data for reactions having small heats of reaction, as the isomerization reaction in question, provide stringent tests for the accuracy of thermodynamic data.

2. Equilibrium Constants for the Dehydrogenation of *n*-Butane(*g*) to *n*-Butenes(*g*) and 1,3-Butadiene(*g*)

From the tables of the preceding sections the equilibrium constants (K_p for pressures in at-

TABLE XI. Entropy, free energy, and related quantities of 1-butene in the ideal gas state at 1 atmosphere pressure. ΔF^0 and K are the free-energy change and equilibrium constant, respectively, for the reaction forming 1-butene from its elements in their standard states at $T^\circ\text{K}$ ($E_0^0 = 5370 \text{ cal mole}^{-1}$).

T °K	$-\left(\frac{F^0 - E_0^0}{T}\right)$ cal. deg. ⁻¹ mole ⁻¹	S^0 cal. deg. ⁻¹ mole ⁻¹	$-F^0$ cal. mole ⁻¹	ΔF^0 cal. mole ⁻¹	$\log_{10} K$ $-\Delta F^0/RT$ 2.3026
298.16	59.47	73.07	12365	17390	-12.745
300.00	59.56	73.20	12500	17490	-12.745
400	63.82	79.91	20160	23440	-12.808
500	67.67	86.26	28460	29740	-12.999
600	71.28	92.27	37400	36240	-13.201
700	74.69	97.96	46910	42910	-13.396
800	77.94	103.33	56980	49670	-13.570
900	81.05	108.42	67580	56500	-13.720
1000	84.03	113.23	78660	63380	-13.851
1100	86.89	117.79	90210	70280	-13.963
1200	89.64	122.12	102200	77210	-14.062
1300	92.30	126.24	114620	84120	-14.143
1400	94.87	130.16	127450	91040	-14.212
1500	97.34	133.90	140640	97980	-14.275

³⁸ F. Runge and M. Mueller-Conradi, U. S. Patent 1,914,674, June 20, 1933.

³⁹ C. D. Hurd and A. R. Goldsby, "Rearrangement during pyrolysis of the butenes," J. Am. Chem. Soc. 56, 1812 (1934).

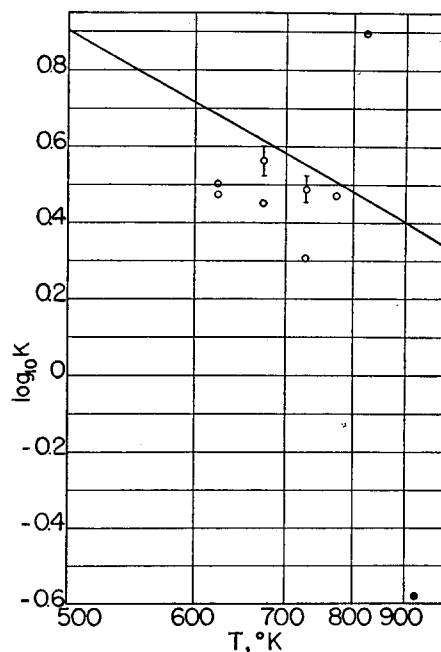


FIG. 3. Logarithm of the equilibrium constant for the isomerization of 1-butene to 2-butene. Scale of abscissas is linear in $1/T$.

○ McCarthy and Turkevich, with their estimated range of error
 ○ Frey and Huppke
 ● Runge and Mueller-Conradi (I. G. Farben)
 ● Hurd and Goldsby.

The curve represents the calculated values of this paper.

mospheres) have been calculated for the four reactions:

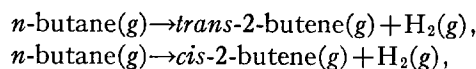
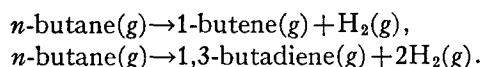


TABLE XII. Equilibrium constants K for the isomerization of 1-butene to 2-butenes: 1-butene \rightarrow 2-butene (*trans*, *cis*, or mixed).

T °K	<i>trans</i> -2-butene	<i>cis</i> -2-butene	mixed-2-butenes
298.16	33.7	9.18	42.9
300.00	32.9	9.08	42.0
400	10.6	4.34	14.9
500	5.31	2.70	8.01
600	3.32	1.90	5.22
700	2.37	1.46	3.83
800	1.85	1.19	3.04
900	1.50	1.01	2.51
1000	1.28	0.881	2.17
1100	1.13	.789	1.92
1200	1.02	.721	1.74
1300	0.931	.665	1.60
1400	.865	.618	1.48
1500	.805	.583	1.39

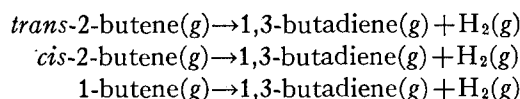


The results are summarized in Table XIII.

Experimental values for the *n*-butane-*n*-butene equilibrium constants were determined by Frey and Huppke.³⁷ A comparison with their values is shown in Table XIV. At the highest temperature, 723°K, the agreement is a little poorer than would be expected on the basis of the experimental accuracy originally claimed by Frey and Huppke. At the lowest temperature, 623°K, the experimental values of K_p are higher than the calculated by approximately the factor two. Considering the small concentrations of components that had to be measured in determining the experimental values it is not surprising that there is a discrepancy between measured and calculated values.

3. Equilibrium Constants for the Dehydrogenation of the *n*-Butenes(*g*) to 1,3-Butadiene(*g*)

Equilibrium constants calculated from our data for the three reactions



are presented in Table XV.

The equilibrium constants for the reaction mixed butenes(*g*) (in equilibrium) \rightarrow 1,3-butadiene(*g*) + $\text{H}_2(g)$ involved when a mixture of *cis*- and *trans*-2-butene and 1-butene is in equilibrium with 1,3-butadiene are given in the last column of Table XV. This constant is calculated from

TABLE XIII. Equilibrium constants for the gas phase dehydrogenation of *n*-butane to butenes or to 1,3-butadiene: *n*-butane \rightarrow butene (or 1,3-butadiene) and hydrogen.

<i>T</i> °K	K_p in atmos.			K_p in atmos. ² 1,3-butadiene
	<i>trans</i> -2-butene	<i>cis</i> -2-butene	1-butene	
298.16	1.09×10^{-14}	2.96×10^{-15}	3.22×10^{-16}	3.52×10^{-30}
300.00	1.44×10^{-14}	3.98×10^{-15}	4.39×10^{-16}	6.31×10^{-30}
400	1.54×10^{-9}	6.32×10^{-10}	1.46×10^{-10}	1.51×10^{-19}
500	1.69×10^{-6}	8.63×10^{-7}	3.19×10^{-7}	3.12×10^{-13}
600	1.89×10^{-4}	1.08×10^{-4}	5.70×10^{-5}	5.74×10^{-9}
700	5.57×10^{-3}	3.44×10^{-3}	2.40×10^{-3}	6.82×10^{-6}
800	7.18×10^{-2}	4.63×10^{-2}	3.89×10^{-2}	1.44×10^{-3}
900	0.518	0.347	0.344	9.33×10^{-2}
1000	2.52	1.73	1.96	2.65
1100	9.25	6.46	8.18	41.3
1200	27.4	19.4	26.9	408
1300	68.9	49.2	74.0	2850
1400	153	109	177	15100
1500	300	217	372	63500

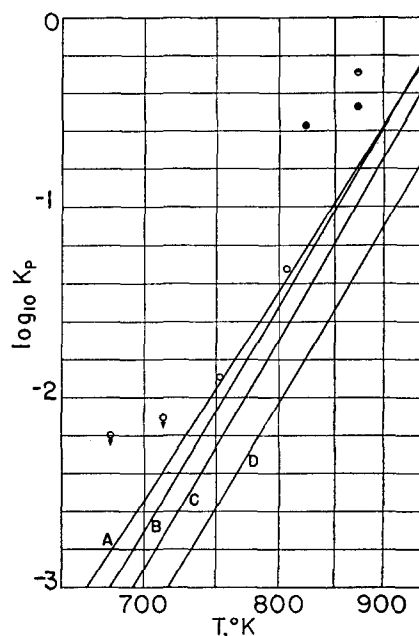


FIG. 4. Equilibrium constants for the dehydrogenation of butenes to butadiene. Scale of abscissas is linear in $1/T$. Curve A—1-butene(*g*) \rightarrow 1,3-butadiene(*g*) + $\text{H}_2(g)$. Curve B—*cis*-2-butene(*g*) \rightarrow 1,3-butadiene(*g*) + $\text{H}_2(g)$. Curve C—*trans*-2-butene(*g*) \rightarrow 1,3-butadiene(*g*) + $\text{H}_2(g)$. Curve D—mixed normal butenes(*g*) \rightarrow 1,3-butadiene(*g*) + $\text{H}_2(g)$. ○—Dementjeva, Frost, and Serebriakova (nature of butenes unspecified). Circles with arrows are reported as upper limits. ●—Balandin, Zelinsky, Bogdanova, and Sceglva (1-butene, compare with curve A). ●—Universal Oil Products (mixed butenes compare with curve D).

the formula

$$\frac{1}{K_{\text{mix}}} = \frac{1}{K_{\text{trans-2}}} + \frac{1}{K_{\text{cis-2}}} + \frac{1}{K_{1-}},$$

where the K 's are the equilibrium constants for

TABLE XIV. A comparison of calculated and experimental^a equilibrium constants for the gas phase dehydrogenation of *n*-butane to butene: *n*-butane \rightarrow butene + hydrogen.

<i>T</i> °K	K_p in atmos.		
	<i>trans</i> -2-butene	<i>cis</i> -2-butene	1-butene
623	obs.	0.00083	0.00052
	calc.	0.00045	0.00026
673	obs.	0.0039	0.0025
	calc.	0.0025	0.0015
723	obs.	0.014	0.0087
	calc.	0.011	0.0067

^a F. E. Frey and W. F. Huppke, Ind. Eng. Chem. 25, 54 (1933).

the separate reactions above. This relation is readily obtained from the fact that the partial pressure of the mixed *n*-butenes is the sum of the partial pressures of the *trans*-2-butene, the *cis*-2-butene and the 1-butene.

The published experimental data for reactions forming 1,3-butadiene from butenes include those of Dementjeva, Frost, and Serebriakova,⁴⁰ Balandin, Zelinsky, Bogdanova, and Sceglava,⁴¹

TABLE XV. Equilibrium constants for the gas phase dehydrogenation of the individual and mixed normal butenes to 1,3-butadiene: butene \rightarrow 1,3-butadiene + hydrogen.

T °K	K _p in atmos.			
	<i>cis</i> -2-butene	<i>trans</i> -2-butene	1-butene	mixed butenes
298.16	1.19×10^{-15}	3.24×10^{-16}	1.09×10^{-14}	2.48×10^{-16}
300.00	1.59×10^{-16}	4.37×10^{-16}	1.44×10^{-14}	3.35×10^{-16}
400	2.38×10^{-10}	9.79×10^{-11}	1.04×10^{-9}	6.50×10^{-11}
500	3.61×10^{-7}	1.84×10^{-7}	9.77×10^{-7}	1.08×10^{-7}
600	5.31×10^{-5}	3.04×10^{-5}	1.01×10^{-4}	1.62×10^{-5}
700	1.98×10^{-3}	1.22×10^{-3}	2.90×10^{-3}	6.00×10^{-4}
800	3.10×10^{-2}	2.00×10^{-2}	3.69×10^{-2}	9.14×10^{-3}
900	0.269	0.180	0.271	7.72×10^{-2}
1000	1.53	1.05	1.35	0.426
1100	6.40	4.47	5.05	1.73
1200	21.1	14.9	15.2	5.54
1300	57.9	41.4	38.6	14.8
1400	138	98.6	85.3	34.4
1500	292	212	171	71.4

⁴⁰ M. I. Dementjeva, A. V. Frost, and E. K. Serebriakova, "Equilibrium dehydrogenation of *n*-butylenes to butadiene $n\text{-C}_4\text{H}_8 \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}_2$," *Comptes rendus (Doklady) Acad. Sci. U.R.S.S.* **15**, 141 (1937).

⁴¹ A. Balandin, N. Zelinsky, O. Bogdanova, A. Sceglava, "Production of divinyl by catalytic dehydrogenation of butylene," *J. App. Chem. U.S.S.R.* **14**, 435 (1941).

and the Universal Oil Products Company.⁴² These data and the calculated equilibrium constants are shown for comparison in Fig. 4 in which values of $\log_{10} K_p$ are plotted against a scale linear in $1/T$.

It is interesting to note that the experimental data are in best agreement with the calculated equilibrium constants for the dehydrogenation of 1-butene to 1,3-butadiene. In the work of Dementjeva *et al.* the composition of the butene was not given; in the work of the Universal Oil Products Company it was described as a mixture of α - and β -butylene (1- and 2-butenes); in the work of Balandin *et al.* it was stated to be α -butylene (1-butene).

It is believed that the calculated values of the 1,3-butadiene-butene equilibria are more reliable than the experimental values. Experimental determinations of equilibrium constants should be made by approaching an equilibrium condition from opposite sides as was done by McCarthy and Turkevich³⁶ for the 1-butene-2-butene equilibrium (see Section VIII-1). Apparently this was not done by the above-mentioned investigators of the 1,3-butadiene-butene equilibria. Chemical analyses of butadiene-butene mixtures are difficult, and there is a question whether the investigators made satisfactory analyses.

⁴² Universal Oil Products Company, "Dehydrogenation of aliphatic hydrocarbons," *Chem. Zentralbl.* **I**, 4262 (1938).