

Equilibrium Constants of Some Reactions Involved in the Production of 1,3-Butadiene¹

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Thermodynamic functions including free energy, enthalpy, entropy, and specific heat, are given for the compounds butadiene, benzene, cyclohexane, ethane, ethylene, ethyl alcohol and water and for the elements carbon (graphite), hydrogen and oxygen. From these are calculated and tabulated values of equilibrium constants for reactions of interest in connection with the production of 1,3-butadiene for synthetic rubber. Comparisons are made between table values and available experimental data on equilibrium constants, gaseous specific heats and entropies. The cracking of hydrocarbons is discussed and the importance of reaction rates in determining the amounts of reaction products is noted.

I. Introduction

In an earlier publication the measured thermal properties of 1,3-butadiene including heat capacities down to 15° K were used to determine the entropy and enthalpy of butadiene to 300° K [1, 2].³ With these calorimetric data and the most recent spectroscopic data, the thermodynamic functions for butadiene were then extended to higher temperatures. These were combined with the thermodynamic functions for *n*-butane and the *n*-butenes to calculate the equilibrium constants for the dehydrogenation reactions of *n*-butane and *n*-butenes used in the manufacture of butadiene from petroleum and natural gas. [3, 4].

In the present paper are given values for thermodynamic functions and properties of a number of other compounds for use in calculations of equilibria occurring in other reactions involved in the commercial production of 1,3-butadiene for synthetic rubber. These compounds are benzene, cyclohexane, ethane, ethylene, ethyl alcohol, and water. Tables for the elements graphite, hydrogen, and oxygen also have been included. Tables

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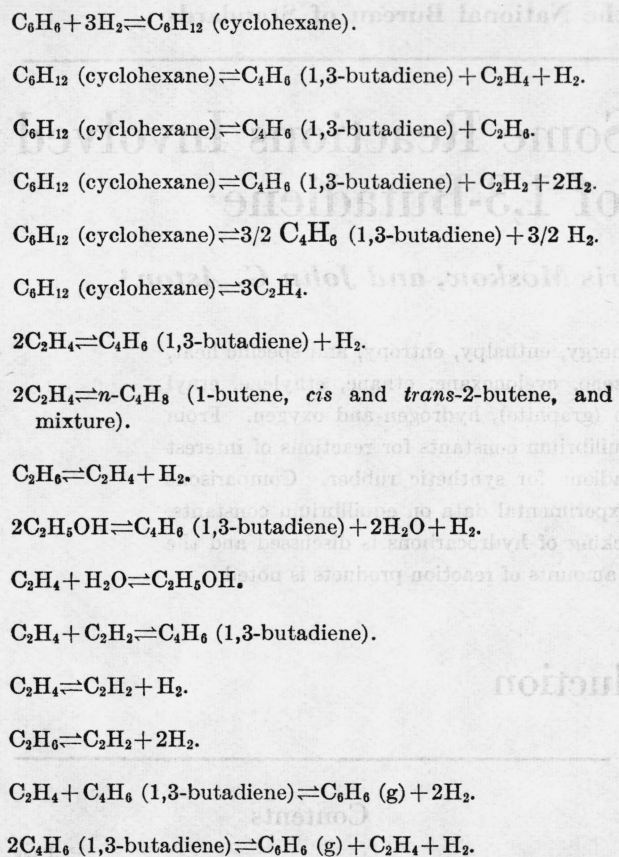
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¹ This paper is a revision of a report entitled, "Equilibrium constants of some reactions involved in the production of 1,3-butadiene," submitted to the Office of the Rubber Director, March 24, 1944.

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³ Figures in brackets indicate literature references at the end of this paper.

of equilibrium constants are given for the following reactions:



The thermodynamic functions and properties of all the substances included in this paper, with the exception of cyclohexane, have been previously

II. Butadiene

Thermodynamic functions for 1,3-butadiene from reference [4] are given in tables 1 and 2. As indicated in that publication, it is concluded that 1,3-butadiene has more than one form, since, for any vibration assignment that seemed reasonable, the specific heat calculated did not agree with the experimental when it was assumed that only a single form existed. Agreement with the experimental calorimetric data was obtained by the use of a *cis* and a *trans* form.

Except for the frequency of torsion about the central C—C bond, the distribution of energy levels has been assumed to be statistically the same for the *cis* as for the *trans* variety. The frequency assignment for the *trans* variety is

calculated and published by others. However, new values for these functions and properties have been calculated for this paper, taking account of the latest spectroscopic and calorimetric data and by using the latest values of the fundamental physical constants.⁴ In a number of cases, the frequency assignments adopted cannot be regarded as certain but appear to be the most reasonable that have been proposed. It is thought that, in general, further improvements in the values taken for the fundamental frequencies given in this paper would result in only small changes of the calculated thermodynamic properties.

The thermodynamic functions and properties are given in tables 1 to 24.⁵ Data and calculations upon which these tables are based are discussed in sections II to XI. Comparisons between calculated and experimental entropies and heat capacities are included for most of the compounds. The heats of formation of the compounds are discussed in section XII. The equilibrium constants of the reactions are given in tables 25 to 29 and are discussed in section XIII. In section XIV the results of some investigations on cracking reactions are compared with theoretically predicted equilibrium concentrations.

⁴ The physical constants include $hc/k=1.4384$ cm deg, $R=1.98714$ artificial cal deg⁻¹ mole⁻¹ or 8.3144×10^7 erg deg⁻¹ mole⁻¹, and $N_0=6.0228 \times 10^{23}$ mole⁻¹, with 1 artificial calorie defined as 4.1833 international joules. The atomic weights used are hydrogen 1.0080, carbon 12.01, and oxygen 16.

⁵ In these tables the following conventions have been adopted: For enthalpy, H° , and for free energy, F° , the quantities are given as values above assumed zeros for the elements in their standard states at 0°K. ΔH° , ΔF° , and K , respectively, are 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 .

mainly that of Bradacs and Kahovec [5]. It differs in the following. The observed Raman line 340 cm⁻¹ that Bradacs and Kohovec assigned, with expressed doubt, to the fundamental of the middle C—C torsional vibration was assigned by us to the first overtone of this vibration. For double-bond torsions the observed 520 cm⁻¹ and a calculated 667 cm⁻¹ based on ethylene have been used. For the skeletal deformation frequency ω_5 , the 520 cm⁻¹ used by Bradacs and Kahovec has been replaced by 326 cm⁻¹ on the basis of force-constant calculations and the calorimetric data. The barrier heights are 5,000 cal mole⁻¹ for the *trans* form and 2,575 cal mole⁻¹ for the *cis* form.

TABLE 1.—Heat capacity at constant pressure, heat content, and related quantities of 1,3-butadiene in the ideal gas state

[$E_0^{\circ}=30,200$ cal mole $^{-1}$]

T	$\frac{H^{\circ}-E_0^{\circ}}{T}$	H°	$^{\circ}\Delta H^{\circ}$	C_p°
$^{\circ}K$	cal deg $^{-1}$ mole $^{-1}$	cal mole $^{-1}$	cal mole $^{-1}$	cal deg $^{-1}$ mole $^{-1}$
298.16	12.16	33,830	26,750	19.01
300.00	12.20	33,860	26,730	19.11
400	14.59	36,040	25,830	24.29
500	16.97	38,690	25,120	28.52
600	19.18	41,710	24,540	31.84
700	21.19	45,040	24,080	34.55
800	23.01	48,610	23,710	36.84
900	24.66	52,390	23,420	38.81
1,000	26.16	56,360	23,210	40.52
1,100	27.54	60,490	23,060	42.02
1,200	28.80	64,760	22,980	43.32
1,300	29.96	69,150	22,940	44.47
1,400	31.03	73,650	22,950	45.47
1,500	32.02	78,240	22,980	46.34

$^{\circ}\Delta H^{\circ}$ is the enthalpy of formation of 1,3-butadiene from its elements in their standard states at the temperature T .

TABLE 2.—Entropy, free energy, and related quantities of 1,3-butadiene in the ideal gas state at 1-atmosphere pressure

[$E_0^{\circ}=30,200$ cal mole $^{-1}$]

T	$-\left(\frac{F^{\circ}-E_0^{\circ}}{T}\right)$	S°	$-F^{\circ}$	$^{\circ}\Delta F^{\circ}$	$^{\circ}\log_{10}K$
$^{\circ}K$	cal deg $^{-1}$ mole $^{-1}$	cal deg $^{-1}$ mole $^{-1}$	cal mole $^{-1}$	cal mole $^{-1}$	$-\frac{\Delta F^{\circ}}{RT}$ 2.3026
298.16	54.46	66.62	-13,960	36,430	-26.707
300.00	54.54	66.74	-13,840	36,490	-26.587
400	58.38	72.97	-6,850	39,890	-21.793
500	61.89	78.86	+740	43,490	-19.009
600	65.18	84.36	8,920	47,210	-17.198
700	68.29	89.48	17,600	51,040	-15.934
800	71.24	94.25	26,790	54,920	-15.003
900	74.05	98.71	36,440	58,830	-14.287
1,000	76.72	102.88	46,520	62,780	-13.721
1,100	79.28	106.82	57,010	66,740	-13.260
1,200	81.73	110.53	67,880	70,720	-12.880
1,300	84.09	114.05	79,110	74,690	-12.557
1,400	86.35	117.38	90,680	78,670	-12.281
1,500	88.52	120.54	102,580	82,660	-12.043

$^{\circ}\Delta F^{\circ}$ 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 $T^{\circ}K$.

III. Benzene

The frequencies assigned to the fundamental modes of vibration of the benzene molecule by K. S. Pitzer and D. W. Scott were used for this paper [6]. These frequencies in centimeters $^{-1}$ are as follows:

Carbon skeleton frequencies:

Vibrations in the plane of the molecule: $\omega_1=\omega_2=606$, $\omega_3=1011$, $\omega_4=992$, $\omega_5=\omega_6=1485$, $\omega_7=\omega_8=1596$, and $\omega_9=(1693)$.

Vibrations out of the plane of the molecule: $\gamma_1=(685)$ and $\gamma_2=\gamma_3=400$.

Frequencies due to CH groups:

γ (CH) waving motions out of the plane of the molecule: (1016), 849(2), 671, and (985)(2).

δ (CH) waving motions in the plane of the molecule: (1298), 1178(2), (1170), and 1037(2).

μ (CH) stretching motions: 3062, 3047(2), 3046, and 3080(2). The frequencies in parentheses have not been observed because the vibrations to which they correspond are optically inactive. The benzene molecule is planar, a regular hexagon with distances between carbon atoms equal to

1.39 Å and distances between carbon and hydrogen atoms of 1.09 Å. The symmetry number is 12. The principal moments of inertia about the center of mass are 292.9×10^{-40} g cm 2 , 146.5×10^{-40} g cm 2 , and 146.5×10^{-40} g cm 2 . Their product is 6.28×10^{-114} g 3 cm 6 .

Calculated values of thermodynamic functions and properties are given in tables 3 and 4. The moderate departures of calculated values of $-(F^{\circ}-E_0^{\circ})/T$, $H^{\circ}-E_0^{\circ}$, and C_p° from those of reference [6] are thought to be due to the use of the latest values for the fundamental physical constants in the present calculations. The source of the value for E_0° used in this paper is given in section XII.

Table values of C_p° are in agreement to within experimental accuracy with values of C_p° derived from the calorimetrically measured heat capacities, which extend over the range 360° to 480°K. This may be seen in figure 7 in the paper by Pitzer and Scott, since the sets of calculated values of C_p° in the two papers are in agreement to within less than the experimental error.

TABLE 3.—Heat capacity at constant pressure, heat content, and related quantities of benzene in the ideal gas state

[$E_0^{\ddagger}=24,000$ cal mole⁻¹]

T	$\frac{H^{\circ}-E_0^{\ddagger}}{T}$	H°	${}^{\circ}\Delta H^{\circ}$	C_p°
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	cal deg ⁻¹ mole ⁻¹
298.16	11.41	27,400	19,820	19.51
300.00	11.46	27,440	19,800	19.65
400	14.41	29,760	18,550	26.74
500	17.50	32,750	17,540	32.80
600	20.48	36,290	16,720	37.74
700	23.24	40,270	16,070	41.75
800	25.76	44,610	15,570	45.06
900	28.07	49,260	15,170	47.82
1,000	30.16	54,160	14,880	50.16
1,100	32.07	59,280	14,680	52.15
1,200	33.82	64,580	14,550	53.85
1,300	35.42	70,040	14,490	55.31
1,400	36.88	75,640	14,490	56.57
1,500	38.23	81,350	14,500	57.66

${}^{\circ}\Delta H^{\circ}$ is the enthalpy of formation of benzene from its elements in their standard states at the temperature T .

TABLE 4.—Entropy, free energy and related quantities of benzene in the ideal gas state at 1-atmosphere pressure

[$E_0^{\ddagger}=24,000$ cal mole⁻¹]

T	$-\left(\frac{F^{\circ}-E_0^{\ddagger}}{T}\right)$	S°	$-F^{\circ}$	${}^{\circ}\Delta F^{\circ}$	${}^{\circ}\log_{10} K$
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	$-\Delta F^{\circ}/RT$
298.16	52.94	64.34	-8,220	31,000	2.3026
300.00	53.01	64.46	-8,100	31,070	-22.725
400	56.70	71.10	-1,320	35,020	-22.634
500	60.25	77.74	+6,120	39,260	-19.132
600	63.70	84.18	14,220	43,680	-17.161
700	67.07	90.31	22,950	48,230	-15.058
800	70.34	96.10	32,270	52,860	-14.442
900	73.51	101.57	42,160	57,550	-13.975
1,000	76.58	106.74	52,580	62,270	-13.610
1,100	79.54	111.61	63,490	67,020	-13.315
1,200	82.41	116.23	74,890	71,790	-13.074
1,300	85.18	120.60	86,730	76,550	-12.869
1,400	87.86	124.74	99,000	81,320	-12.695
1,500	90.45	128.68	111,670	86,100	-12.545

${}^{\circ}\Delta F^{\circ}$ and K are the free-energy change and equilibrium constant, respectively, for the reaction forming benzene from its elements in their standard states at $T^{\circ}K$.

IV. Cyclohexane

The frequency assignment used in the calculations for cyclohexane is essentially the same as one given previously [7]. A value of 673 cm⁻¹, which was used in a previous form of this paper for one frequency, has now been replaced by 864 cm⁻¹ on the ground that the band reported at 673 cm⁻¹ was due to an impurity.⁶ The molecule has a chair form with D_{3d} symmetry, for which the symmetry number is 6. The frequencies in cm⁻¹ used were as follows:

Carbon skeleton frequencies:

Vibrations essentially parallel to the σ_2 plane: $\omega_1 = \omega_2 = 425$, $\omega_3 = 864$, $\omega_4 = 801$, $\omega_5 = \omega_6 = 1050$, $\omega_7 = \omega_8 = 1266$, and $\omega_9 = 1370$.

Vibrations essentially parallel to the principal axis [C_3] of the molecule: $\gamma_1 = \gamma_2 = 196$ and $\gamma_3 = 377$.

Frequencies due to CH₂ groups:

$\gamma(\text{CH}_2)$ waving motions: 885(6), 1028(6), and 1345(6).

$\delta(\text{HCH})$ bending motions: 1300(6).

$\nu(\text{CH})$ stretching motions: 2770(12).

The frequency of the optically inactive, and doubly degenerate, rocking motion of the carbon skeleton, $\gamma_1 = \gamma_2$, was calculated from the calorimetrically determined entropy [8] by using the assignments given here for the remaining frequencies.

⁶ A private communication from E. K. Plyler, of the Radiometry Section of the National Bureau of Standards, indicates that there is no evidence for a band at 673 cm⁻¹ when a very pure sample of cyclohexane is used.

The distance between carbon atoms was taken as 1.54 Å and between carbon and hydrogen atoms as 1.09 Å. Using tetrahedral angles, the principal moments of inertia are 335.1×10^{-40} g cm², 193.8×10^{-40} g cm², and 193.8×10^{-40} g cm², giving for the product of the three 12.58×10^{-114} g³ cm⁶.

Tables 5 and 6 give the calculated values of

TABLE 5.—Heat capacity and constant pressure, heat content, and related quantities of cyclohexane in the ideal gas state

[$E_0^{\ddagger}=19,950$ cal mole⁻¹]

T	$\frac{H^{\circ}-E_0^{\ddagger}}{T}$	H°	${}^{\circ}\Delta H^{\circ}$	C_p°
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	cal deg ⁻¹ mole ⁻¹
298.16	14.13	-15,740	-29,380	25.15
300.00	14.20	-15,690	-29,440	25.35
400	18.31	-12,630	-32,030	35.87
500	22.80	-8,550	-34,050	45.42
600	27.26	-3,590	-35,550	53.45
700	31.50	+2,100	-36,590	60.15
800	35.44	8,400	-37,260	65.77
900	39.08	15,220	-37,610	70.50
1,000	42.43	22,480	-37,700	74.51
1,100	45.50	30,100	-37,580	77.92
1,200	48.33	38,040	-37,270	80.82
1,300	50.93	46,250	-36,820	83.30
1,400	53.31	54,690	-36,250	85.42
1,500	55.52	63,330	-35,610	87.26

${}^{\circ}\Delta H^{\circ}$ is the enthalpy of formation of cyclohexane from its elements in their standard states at the temperature T .

TABLE 6.—Entropy, free energy, and related quantities of cyclohexane in the ideal gas state at 1-atmosphere pressure

[$E_0^\circ = 19,950$ cal mole⁻¹]

T	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	S°	$-F^\circ$	ΔF°	$\log_{10} K$
$^\circ K$	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	$\frac{\Delta F^\circ}{RT}$
298.16	57.28	71.41	37,030	7,600	-5.570
300.00	57.37	71.57	37,160	7,830	-5.703
400	62.00	80.31	44,750	20,650	-11.283
500	66.57	89.37	53,230	34,070	-14.894
600	71.12	98.38	62,620	47,840	-17.426
700	75.64	107.14	72,900	61,830	-19.305
800	80.11	115.55	84,040	75,950	-20.748
900	84.50	123.58	96,000	90,120	-21.884
1,000	88.79	131.22	108,740	104,310	-22.798
1,100	92.98	138.48	122,230	118,510	-23.545
1,200	97.06	145.39	136,420	132,690	-24.166
1,300	101.03	151.96	151,290	146,820	-24.683
1,400	104.90	158.21	166,800	160,920	-25.121
1,500	108.65	164.17	182,930	175,000	-25.498

ΔF° and K are the free-energy change and equilibrium constant, respectively, for the reaction forming cyclohexane from its elements in their standard states at $T^\circ K$.

thermodynamic functions and properties. Table 7 is a comparison of calculated values and the experimental values of C_p° of Montgomery and DeVries [8] and Bennewitz and Rossner [9].

In section XIV the calculated values for the equilibrium constant for the hydrogenation of benzene to cyclohexane are compared with experimental data. The agreement is considered satisfactory.

TABLE 7.—A comparison of the calculated and experimental values for the heat capacity of cyclohexane above 300° K

T	C_p° (calculated)	C_p° (experimental)	Observers ^a
$^\circ K$	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	
370	32.80	33.0	(8)
390	34.86	35.0	(8)
410	36.88	36.8	(8)
410	36.88	37.0	(9)

^a(8) J. B. Montgomery and T. DeVries, (9) K. Bennewitz and W. Rossner,

V. Ethane

The frequency assignment used for ethane was taken from a paper by Stitt [10]. The frequencies in centimeters⁻¹ were:

Frequency due to C—C vibration:

$$\omega = 993.$$

Frequencies due to CH₃ vibrations:

γ (CH₃) rocking motions: 827(2) and 1170(2).

δ (HCH) bending motions: 1375, 1380, 1460(2), and 1465(2).

μ (C—H) stretching motions: 2925(2), 2960(2), and 2980(2).

Stitt's value of 1,170 cm⁻¹ for the "uncertain frequency" of ethane is based upon D_{3d} symmetry and an application of the product rule to the spectra of C₂H₆ and C₂D₆.

As Kemp and Pitzer [11] have shown and others have confirmed, there is a mode of hindered rotation corresponding to rotation of one methyl group with respect to the other. For low energies the motion is vibration, whereas for large energies it is complete rotation. The height used for the barrier, 2,750 cal mole⁻¹, is the value

determined by Kistiakowsky, Lacher, and Stitt [12] from low-temperature specific-heat measurement on gaseous ethane.

The ethane molecule has a symmetry number of six. With 1.54 Å for the carbon-carbon distance and 1.09 Å for the carbon-hydrogen distances, the principal moments of inertia are found to be 10.60×10^{-40} g cm², 41.84×10^{-40} g cm², and 41.84×10^{-40} g cm², whereas the reduced moment for the internal rotation is 2.65×10^{-40} g cm². The product of the principal moments of inertia is 18.56×10^{-117} g³ cm⁶.

The values calculated for the various thermodynamic functions of ethane are given in tables 8 and 9.

Table 10 gives a comparison of calculated values of C_p° with experimental values based on the work of Thayer and Stegeman [13], Dailey and Felsing [14] and Eucken and Parts [15].

The calorimetric entropy, S° , at 25° C is given by Witt and Kemp [16] as 54.85 cal deg⁻¹ mole⁻¹. The corresponding statistically calculated S° for 298.16° K is 54.83 cal deg⁻¹ mole⁻¹.

TABLE 8.—Heat capacity at constant pressure, heat content, and related quantities of ethane in the ideal gas state

[$E_0^{\circ} = -16,520$ cal mole⁻¹]

T	$\frac{H^{\circ} - E_0^{\circ}}{T}$	H°	$^{\circ}\Delta H^{\circ}$	C_p°
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	cal deg ⁻¹ mole ⁻¹
298.16	9.59	-13,660	-20,240	12.59
300.00	9.60	-13,640	-20,260	12.65
400	10.73	-12,230	-21,430	15.68
500	12.02	-10,510	-22,440	18.66
600	13.35	-8,510	-23,290	21.34
700	14.67	-6,250	-23,980	23.71
800	15.93	-3,780	-24,530	25.82
900	17.13	-1,100	-24,960	27.68
1,000	18.27	+1,750	-25,280	29.31
1,100	19.34	4,750	-25,500	30.75
1,200	20.33	7,880	-25,650	32.00
1,300	21.27	11,130	-25,730	33.10
1,400	22.15	14,480	-25,760	34.05
1,500	22.97	17,930	-25,750	34.89

$^{\circ}\Delta H^{\circ}$ is the enthalpy of formation of ethane from its elements in their standard states at the temperature T .

TABLE 9.—Entropy, free energy, and related quantities of ethane in the ideal gas state at 1-atmosphere pressure

[$E_0^{\circ} = -16,520$ cal mole⁻¹]

T	$-\left(\frac{F^{\circ} - E_0^{\circ}}{T}\right)$	S°	$-F^{\circ}$	$^{\circ}\Delta F^{\circ}$	$^{\circ}\log_{10}K$
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	$\frac{F^{\circ}/RT}{2.3026}$
298.16	45.25	54.83	30,010	-7,850	5.756
300.00	45.31	54.91	30,110	-7,780	5.665
400	48.22	58.95	35,810	-3,440	1.880
500	50.76	62.78	41,900	+1,180	-0.514
600	53.07	66.42	48,360	5,980	-2.179
700	55.22	69.89	55,180	10,920	-3.409
800	57.27	73.20	62,330	15,940	-4.356
900	59.21	76.34	69,810	21,030	-5.106
1,000	61.08	79.35	77,600	26,150	-5.715
1,100	62.87	82.21	85,680	31,310	-6.220
1,200	64.60	84.93	94,040	36,480	-6.643
1,300	66.27	87.54	102,670	41,650	-7.001
1,400	67.88	90.03	111,560	46,820	-7.309
1,500	69.44	92.41	120,680	52,010	-7.577

$^{\circ}\Delta F^{\circ}$ and K are the free-energy change and equilibrium constant, respectively, for the reaction forming ethane from its elements in their standard states at $T^{\circ}K$.

TABLE 10.—Comparison of the calculated and experimental values for the heat capacity of ethane in the ideal gas state (above 300° K)

T	C_p° (calculated)	C_p° (experimental)	Observers *
$^{\circ}K$	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	
337.66	13.78	13.3	(13)
347.66	14.09	14.08	(14)
359.76	14.46	14.43	(14)
373.5	14.87	14.836	(15)
373.6	14.88	14.842	(15)
387.56	15.30	15.27	(14)
451.96	17.26	17.31	(14)
520.56	19.24	19.14	(14)
561.66	20.36	20.62	(14)
603.26	21.42	21.62	(14)

* (13) V. R. Thayer and G. Stegeman, (14) B. P. Dailey and W. A. Felsing, (15) A. Eucken and A. Parts.

VI. Ethylene

The fundamental frequencies used for ethylene are those given by Galloway and Barker [17]. The frequencies in centimeters⁻¹ are:

Frequency due to C=C vibration:

1623.3

Frequencies due to CH₂ vibrations:

γ (C—H) rocking motions: 995, 1055, 949.2, 950, and 825.

δ (HCH) bending motions: 1342.4 and 1443.9.
 μ (C—H) stretching motions: 3019.3, 2989.5, 3105.5, and 3069. The frequency 825 cm⁻¹ corresponds to the torsional twist of the C=C bond.

The molecule is planar and has a symmetry number of 4. The principal moments of inertia derived from the ethylene spectra by Galloway and Barker were used. They are 33.84×10^{-40} g cm²,

28.09×10^{-40} g cm², and 5.750×10^{-40} g cm². Their product is 5.466×10^{-117} g³ cm⁶. The thermodynamic functions for ethylene are given in tables 11 and 12.

In table 13 the calculated values of C_p° are compared with the experimental values from the work of Haas and Stegeman [18], Burcik, Eyster, and Yost [19] and Eucken and Parts [15].

The calorimetric entropy, S° , at 25° C, is given by Egan and Kemp [20] as 52.48 cal deg⁻¹ mole⁻¹. The corresponding statistically calculated S° for 298.16°K is 52.454 cal deg⁻¹ mole⁻¹.

TABLE 11.—Heat capacity at constant pressure, heat content and related quantities of ethylene in the ideal gas state

[$E_0^\circ = 14,530$ cal mole⁻¹]

T	$\frac{H^\circ - E_0^\circ}{T}$	H°	$^\circ \Delta H^\circ$	C_p°
°K	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	cal deg ⁻¹ mole ⁻¹
298.16	8.47	17,060	12,510	10.41
300.00	8.49	17,080	12,490	10.46
400	9.28	18,240	11,780	12.91
500	10.24	19,650	11,150	15.18
600	11.23	21,270	10,610	17.12
700	12.19	23,070	10,170	18.78
800	13.11	25,020	9,800	20.23
900	13.97	27,110	9,490	21.49
1,000	14.78	29,310	9,250	22.60
1,100	15.54	31,620	9,060	23.58
1,200	16.25	34,020	8,920	24.43
1,300	16.90	36,500	8,810	25.18
1,400	17.52	39,050	8,740	25.83
1,500	18.09	41,670	8,690	26.41

$^\circ \Delta H^\circ$ is the enthalpy of formation of ethylene from its elements in their standard states at the temperature T .

TABLE 12.—Entropy, free energy, and related quantities of ethylene in the ideal gas state at 1-atmosphere pressure

[$E_0^\circ = 14,530$ cal mole⁻¹]

T	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	S°	$-F^\circ$	$^\circ \Delta F^\circ$	$^\circ \log_{10} K$
°K	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	cal mole ⁻¹	cal mole ⁻¹	$-\frac{\Delta F^\circ}{RT}$
298.16	43.98	52.45	-1,420	16,290	-11.943
300.00	44.03	52.52	-1,320	16,320	-11.887
400	46.58	55.86	+4,100	17,700	-9.670
500	48.75	58.99	9,850	19,260	-8.417
600	50.71	61.94	15,890	20,930	-7.613
700	52.51	64.70	22,230	22,680	-7.082
800	54.20	67.31	28,830	24,500	-6.693
900	55.79	69.76	35,680	26,350	-6.400
1,000	57.31	72.09	42,780	28,240	-6.172
1,100	58.75	74.29	50,100	30,150	-5.990
1,200	60.13	76.38	57,630	32,070	-5.841
1,300	61.46	78.36	65,370	34,000	-5.717
1,400	62.73	80.25	73,300	35,940	-5.611
1,500	63.96	82.05	81,420	37,890	-5.520

$^\circ \Delta F^\circ$ and K are the free-energy change and equilibrium constant, respectively, for the reaction forming ethylene from its elements in their standard states at T° K.

TABLE 13.—Comparison of the calculated and experimental values for the heat capacity of ethylene in the ideal gas state above 300° K

T	C_p° (calculated)	C_p° (experimental)	Observers ^a
°K	cal deg ⁻¹ mole ⁻¹	cal deg ⁻¹ mole ⁻¹	
298.16	10.41	9.97	(18)
319.16	10.98	10.40	(18)
339.96	11.46	10.98	(18)
300.0	10.46	10.39	(19)
320.7	11.00	10.99	(19)
368.2	12.15	11.897	(15)
464.0	14.39	14.16	(15)

^a (18) M. E. Haas and G. Stegeman, (19) E. J. Burcik, E. H. Eyster and D. M. Yost, (15) A. Eucken and A. Parts.

VII. Acetylene

For acetylene, the thermodynamic functions used are those given in a recent paper by Wagman, Kilpatrick, Pitzer, and Rossini [21]. Their values are based largely upon an assignment by Wu [22] and include the effects of anharmonicity, rota-

tional-vibrational coupling, rotational stretching, and an Euler-Maclaurin series summation correction term. They have been used in preference to our earlier tables, which were based on a table by Gordon [23].

VIII. Ethyl Alcohol

The thermodynamic functions for ethyl alcohol are given in tables 14 and 15. The frequency assignment used in the calculations of these tables agrees closely with one previously given [24, 25]. The value of 700 cm^{-1} , there assigned to the COH angle frequency, was based on earlier papers on methyl alcohol. For the COH angle vibration in methyl alcohol, Borden and Barker [26] later suggested a frequency of $1,030\text{ cm}^{-1}$, and most recently Noether [27] assigned the frequency $1,340\text{ cm}^{-1}$. For the calculations of tables 14 and 15 the observed [28] Raman frequency $1,274\text{ cm}^{-1}$ of ethyl alcohol has been assigned to the COH vibration. To the internal bending vibration of the CH_2 group has been assigned the observed Raman frequency $1,455\text{ cm}^{-1}$. Others of the observed Raman frequencies in addition to those listed by Bolla as fundamentals have here been chosen as fundamentals because of their approximate equality with frequencies for similar motions in propane given in the assignment of V. L. Wu and E. F. Barker [29]. Thus the frequencies in centimeters⁻¹ that have been used are:

C-C-O skeleton frequencies:

883, 1096, and 433.

Frequencies due to CH_3 vibrations:

$\gamma(\text{CH}_3)$ rocking motions: 814 and 1051.

$\nu(\text{C-H})$ stretching motions: 2930(3).

$\delta(\text{HCH})$ bending motions: 1387 and 1455(2).

TABLE 14.—Heat capacity at constant pressure, heat content, and related quantities of ethyl alcohol in the ideal gas state

[$E_0^\circ = -52,260\text{ cal mole}^{-1}$]

T	$\frac{H^\circ - E_0^\circ}{T}$	H°	ΔH°	C_p
$^\circ\text{K}$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}	cal mole^{-1}	$\text{cal deg}^{-1}\text{mole}^{-1}$
298.16	12.18	-48,630	-56,240	17.59
300.00	12.22	-48,600	-56,260	17.66
400	14.00	-46,660	-57,250	21.00
500	15.70	-44,410	-58,110	24.09
600	17.33	-41,860	-58,780	26.81
700	18.86	-39,060	-59,320	29.18
800	20.28	-36,030	-59,710	31.25
900	21.61	-32,810	-60,000	33.07
1,000	22.83	-29,430	-60,200	34.66
1,100	23.97	-25,900	-60,320	36.06
1,200	25.02	-22,240	-60,370	37.28
1,300	25.99	-18,470	-60,350	38.34
1,400	26.91	-14,590	-60,250	39.27
1,500	27.75	-10,630	-60,190	40.08

* ΔH° is the enthalpy of formation of ethyl alcohol from its elements in their standard states at the temperature T .

TABLE 15.—Entropy, free energy, and related quantities of ethyl alcohol in the ideal gas state at 1-atmosphere pressure

[$E_0^\circ = -52,260\text{ cal mole}^{-1}$]

T	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	S°	$-F^\circ$	ΔF°	$\log_{10} K$
$^\circ\text{K}$	$\text{cal deg}^{-1}\text{mole}^{-1}$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}	cal mole^{-1}	$-\Delta F^\circ/RT$
298.16	54.27	66.45	68,440	-40,010	2.3026
300.00	54.34	66.56	68,560	-39,910	29.329
400	58.11	72.11	75,500	-34,310	29.075
500	61.42	77.12	82,970	-28,470	18.749
600	64.43	81.76	90,920	-22,490	12.447
700	67.22	86.08	99,310	-16,390	8.191
800	69.84	90.12	108,130	-10,230	5.118
900	72.31	93.92	117,330	-4,030	2.796
1,000	74.65	97.48	126,910	+2,190	0.980
1,100	76.88	100.85	136,830	8,430	-0.479
1,200	79.02	104.04	147,080	14,680	-1.675
1,300	81.07	107.06	157,650	20,920	-2.673
1,400	83.03	109.94	168,500	27,170	-3.517
1,500	84.92	112.67	179,640	33,410	-4.239
					-4.867

* ΔF° and K are the free-energy change and equilibrium constant, respectively, for the reaction forming ethyl alcohol from its elements in their standard states at $T^\circ\text{K}$.

Frequencies due to CH_2 vibrations:

$\gamma(\text{CH}_2)$ waving motions: 814, 1125, and 1160.

$\nu(\text{C-H})$ stretching motions: 2930(2).

$\delta(\text{HCH})$ bending motion: 1455.

Frequencies due to OH vibrations:

$\gamma(\text{O-H})$ stretching motion: 3359.

$\delta(\text{COH})$ bending motion: 1274.

The barriers restricting the internal rotations of ethyl alcohol have recently been estimated [30] by a method involving a correlation of known barrier heights in various compounds. According to this calculation, there is a barrier of $1,800\text{ cal mole}^{-1}$ for the methyl group for the straight form of the molecule, that is, the form in which the OH group is in a plane of symmetry of the molecule, and $3,000\text{ cal mole}^{-1}$ for the bent forms, in which the H of the OH group is on either side of the plane and about 104° from its straight position. The barrier heights for the hydroxyl group are more complicated. For the methyl group in a position of minimum energy the calculated potential energy of the hydroxyl group ranges from zero for the straight form to a maximum of $2,375\text{ cal mole}^{-1}$ when the OH group has rotated about 65° , to a minimum of $1,560\text{ cal mole}^{-1}$ at 104° , to another maximum of $5,970\text{ cal mole}^{-1}$ at 180° , in which

position the OH group extends toward the methyl group.

The calculations of the thermodynamic functions with these data on the barriers restricting rotation have been made by using a natural extension of Pitzer's [31] steric factor method for barriers with different minimal and maximal values.

With 1.54 Å for the C-C distance, 1.09 Å for the C-H distances, 1.42 Å for the C-O distance, 0.96 Å for the O-H distance, 105° for the C-O-H angle and tetrahedral angles for all other angles, the product of the three principal moments of inertia is found to be $2.249 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ for the molecule in the straight form and $2.292 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ for the molecule in the bent form. The reduced moment of inertia for the CH_3 group is $4.83 \times 10^{-40} \text{ g cm}^2$ and for the OH group is $1.40 \times 10^{-40} \text{ g cm}^2$. In table 16 the calculated values of C_p° are compared with the experimental values by Dixon and Greenwood [32], Jatkar [33], Bennewitz and Rossner [9], and Regnault [34]. The calculated values are higher than the experimental values except for the value of Regnault at 623° K. This one value may be doubted because of its antiquity and the experimental difficulties at the elevated temperature. It is entirely possible that the present treatment will require revision

when more accurate experimental values of the specific heat are available.

TABLE 16.—Comparison of the calculated and experimental values for the heat capacity of ethyl alcohol in the ideal gas state

T	C_p° (calculated)	C_p° (experimental)	Observers ^a
° K	<i>cal deg</i> ⁻¹ <i>mole</i> ⁻¹	<i>cal deg</i> ⁻¹ <i>mole</i> ⁻¹	
363.16	19.76	18.49	(32)
370.26	20.00	19.86	(33)
407.16	21.24	18.75	(33)
410.16	21.34	19.6	(9)
437.16	22.20	20.8	(34)
623.16	27.38	28.2	(34)

^a (32) H. B. Dixon and G. Greenwood, (33) S. K. K. Jatkar, (9) K. Bennewitz and W. Rossner, (34) H. V. Regnault.

The entropy, S° , at the boiling point, 351.5° K, based on calorimetric measurements below 298.16° K by Kelley [35] and at higher temperatures by Fiock, Ginnings, and Holton [36] is 69.7 cal deg⁻¹ mole⁻¹. The value interpolated from table 15 is 69.42 cal deg⁻¹ mole⁻¹, agreeing to the uncertainty of the calorimetric value. A similarly obtained calorimetric value of S° at 403.2° K is 72.1 cal deg⁻¹ mole⁻¹, while the corresponding value from table 15 is 72.28 cal deg⁻¹ mole⁻¹.

IX. Water

The thermodynamic functions of table 17 and 18 for water are based on tables published by Gordon [37]. Gordon took into account the anharmonicities of the H_2O vibrations. For the tables of this paper Gordon's values have been adjusted for rotational stretching by using Wilson's theory [38], with a value of the stretching constant determined by Stephenson and McMahon [39]. An adjustment for the change in the generally

accepted values of the fundamental physical constants has also been made.

The entropy, S° , of water at 25° C, was given by Giauque and Archibald [40] as 45.10 cal deg⁻¹ mole⁻¹ on the basis of an investigation of the equilibrium of MgO , $\text{Mg}(\text{OH})_2$, and H_2O , and the calorimetrically determined entropies of MgO and $\text{Mg}(\text{OH})_2$. The value from table 18 is 45.109 cal deg⁻¹ mole⁻¹ at 298.16° K.

TABLE 17.—Heat capacity at constant pressure, heat content, and related quantities of water in the ideal gas state

[$E_0^{\circ} = -57,106 \text{ cal mole}^{-1}$]

T	$\frac{H^{\circ} - E_0^{\circ}}{T}$	H°	$^{\circ}\Delta H^{\circ}$	C_p°
$^{\circ}K$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}	cal mole^{-1}	$\text{cal deg}^{-1}\text{mole}^{-1}$
298.16	7.934	-54,740	-57,799	8.028
300.00	7.935	-54,725	-57,803	8.030
400	7.977	-53,915	-58,042	8.190
500	8.041	-53,085	-58,276	8.421
600	8.125	-52,231	-58,500	8.685
700	8.226	-51,347	-58,707	8.968
800	8.338	-50,436	-58,900	9.264
900	8.456	-49,495	-59,077	9.570
1,000	8.586	-48,520	-59,234	9.881
1,100	8.715	-47,520	-59,379	10.185
1,200	8.851	-46,486	-59,506	10.480
1,300	8.988	-45,422	-59,615	10.763
1,400	9.125	-44,333	-59,715	11.031
1,500	9.260	-43,217	-59,801	11.279

$^{\circ}\Delta H^{\circ}$ is the enthalpy of formation of water from its elements in their standard states at the temperature T .

TABLE 18.—Entropy, free energy and related quantities of water in the ideal gas state at 1-atmosphere pressure

[$E_0^{\circ} = -57,106 \text{ cal mole}^{-1}$]

T	$-\left(\frac{F^{\circ} - E_0^{\circ}}{T}\right)$	S°	$-F^{\circ}$	$^{\circ}\Delta F^{\circ}$	$^{\circ}\log_{10}K$
$^{\circ}K$	$\text{cal deg}^{-1}\text{mole}^{-1}$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}	cal mole^{-1}	$-\frac{\Delta F^{\circ}}{RT}$
298.16	37.175	45.109	68,190	-54,638	40.050
300.00	37.224	45.159	68,273	-54,618	39.790
400	39.512	47.489	72,911	-53,521	29.243
500	41.299	49.340	77,756	-52,363	22.888
600	42.773	50.898	82,770	-51,160	18.635
700	44.032	52.258	87,928	-49,918	15.585
800	45.137	53.475	93,216	-48,648	13.290
900	46.127	54.583	98,620	-47,357	11.500
1,000	47.023	55.609	104,129	-46,046	10.063
1,100	47.849	56.564	109,740	-44,722	8.886
1,200	48.612	57.463	115,440	-43,381	7.901
1,300	49.326	58.314	121,230	-42,036	7.067
1,400	49.997	59.122	127,102	-40,681	6.351
1,500	50.631	59.891	133,052	-39,314	5.728

$^{\circ}\Delta F^{\circ}$ and K are the free-energy change and equilibrium constant, respectively, for the reaction forming water from its elements in their standard states at $T^{\circ}K$.

X. Graphite

The thermodynamic functions for graphite are given in tables 19 and 20. They were obtained by tabular integration of the specific heat of graphite which has been measured [41, 42, 43, 44, 45] within the range -244 to $1,200^{\circ}C$. The values used for specific heats at the higher temperatures were also based in part on specific-heat measurements [46] on a carbon filament from $1,200^{\circ}$ to $2,100^{\circ}C$.

TABLE 19.—Heat capacity at constant pressure, heat content, and $(H^{\circ} - E_0^{\circ})/T$ for graphite

[$E_0^{\circ} = 0$]

T	$\frac{H^{\circ} - E_0^{\circ}}{T}$	H°	C_p°
$^{\circ}K$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}	$\text{cal deg}^{-1}\text{mole}^{-1}$
298.16	0.842	251	2.055
300.00	.850	255	2.071
400	1.258	503	2.852
500	1.642	821	3.488
600	1.993	1,196	3.991
700	2.309	1,616	4.391
800	2.590	2,072	4.720
900	2.841	2,557	4.972
1,000	3.064	3,064	5.159
1,100	3.262	3,588	5.300
1,200	3.437	4,124	5.422
1,300	3.593	4,671	5.520
1,400	3.734	5,227	5.609
1,500	3.862	5,793	5.699

TABLE 20.—Entropy, free energy, and the free-energy function for graphite

[$E_0^{\circ} = 0$]

T	$-\left(\frac{F^{\circ} - E_0^{\circ}}{T}\right)$	S°	$-F^{\circ}$
$^{\circ}K$	$\text{cal deg}^{-1}\text{mole}^{-1}$	$\text{cal deg}^{-1}\text{mole}^{-1}$	cal mole^{-1}
298.16	0.525	1.367	157
300.00	0.529	1.379	159
400	.830	2.088	332
500	1.153	2.795	577
600	1.484	3.477	890
700	1.815	4.124	1,271
800	2.142	4.732	1,714
900	2.462	5.303	2,216
1,000	2.774	5.838	2,774
1,100	3.075	6.337	3,382
1,200	3.367	6.804	4,040
1,300	3.648	7.241	4,742
1,400	3.919	7.653	5,487
1,500	4.181	8.043	6,272

XI. Hydrogen

The thermodynamic functions for hydrogen given in tables 21 and 22 are from an unpublished

compilation of thermal properties of hydrogen [47].

TABLE 21.—Heat capacity at constant pressure, heat content, and related quantities of hydrogen in the ideal gas state

[$E_0^0=0$]

T	$\frac{H^\circ - E_0^0}{T}$	H°	C_p°
$^\circ K$	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal mole⁻¹</i>	<i>cal deg⁻¹ mole⁻¹</i>
298.16	6.787	2023.8	6.891
300.00	6.788	2036.4	6.894
400	6.827	2731.0	6.975
500	6.859	3429.5	6.993
600	6.883	4129.5	7.009
700	6.902	4831.7	7.036
800	6.922	5537.3	7.081
900	6.943	6248.3	7.142
1,000	6.966	6966.2	7.219
1,100	6.993	7,692	7.307
1,200	7.023	8,428	7.406
1,300	7.057	9,174	7.511
1,400	7.093	9,930	7.617
1,500	7.131	10,697	7.720

TABLE 22.—Entropy^a, free energy^a, and related quantities of hydrogen in the ideal gas state at 1-atmosphere pressure

[$E_0^0=0$]

T	$-\left(\frac{F^\circ - E_0^0}{T}\right)$	S°	$-F^\circ$
$^\circ K$	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal mole⁻¹</i>
298.16	24.420	31.207	7.281
300.00	24.462	31.250	7.339
400	26.420	33.247	10.568
500	27.947	34.806	13.974
600	29.200	36.083	17.520
700	30.263	37.165	21.184
800	31.187	38.109	24.950
900	32.003	38.946	28.803
1,000	32.735	39.701	32.735
1,100	33.400	40.393	36.740
1,200	34.010	41.033	40.812
1,300	34.572	41.629	44.944
1,400	35.096	42.189	49.134
1,500	35.588	42.719	53.382

^aThe nuclear spin entropy has been subtracted so that these values may be used directly in connection with chemical reactions.

XII. Oxygen

Thermodynamic functions for oxygen are given in tables 23 and 24. These are based on the tables of Johnston and Walker [48] but have been adjusted to be consistent with a more recent value of Curry and Herzberg [49] for the vibrational frequency and with present generally accepted values of the fundamental physical constants. Curry and Herzberg represented the term values in cm^{-1} of the vibrational levels, with quantum number v ,

relative to the lowest vibrational level ($v=0$) by the formula

$$(1568.33v - 11.993v^2 + 0.0517v^3 - 0.00143v^4).$$

The earlier, or 1933, tables of Johnston and Walker, from which the tables of this paper were obtained by adjustment, were based on the formula

$$(1565.37v - 11.37v^2).$$

TABLE 23.—Heat capacity at constant pressure, heat content and related quantities of oxygen in the ideal gas state

[$E_0^0=0$]

T	$\frac{H^\circ - E_0^0}{T}$	H°	C_p°
$^\circ K$	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal mole⁻¹</i>	<i>cal deg⁻¹ mole⁻¹</i>
298.16	6.941	2,069.8	7.019
300.00	6.942	2,082.7	7.021
400	6.981	2,792.6	7.194
500	7.047	3,523.5	7.430
600	7.131	4,278.6	7.669
700	7.223	5,056.4	7.882
800	7.317	5,853.8	8.062
900	7.409	6,667.7	8.211
1,000	7.495	7,495.3	8.335
1,100	7.576	8,334	8.439
1,200	7.652	9,183	8.528
1,300	7.723	10,040	8.606
1,400	7.789	10,904	8.675
1,500	7.849	11,774	8.739

TABLE 24.—Entropy, free energy, and related quantities of oxygen in the ideal gas state at 1-atmosphere pressure

[$E_0^0=0$]

T	$-\left(\frac{F^\circ - E_0^0}{T}\right)$	S°	$-F^\circ$
$^\circ K$	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal deg⁻¹ mole⁻¹</i>	<i>cal mole⁻¹</i>
298.16	42.067	49.008	12.543
300.00	42.110	49.052	12.633
400	44.112	51.093	17.645
500	45.676	52.723	22.838
600	46.968	54.099	28.181
700	48.074	55.297	33.652
800	49.045	56.362	39.236
900	49.911	57.320	44.920
1,000	50.697	58.192	50.697
1,100	51.415	58.991	56.556
1,200	52.078	59.730	62.494
1,300	52.692	60.415	68.501
1,400	53.267	61.056	74.574
1,500	53.808	61.657	80.712

XIII. Heats of Formation at 0°K

The heats of formation at 0°K, E_0° , given in the tables of this paper were obtained from values of heats of formation at ordinary temperatures.

The calculation of E_0° for 1,3-butadiene is discussed in reference [4].

The heats of formation of the other substances at 298.16°K were based on values published or privately communicated by Rossini and his co-

workers [50, 51, 52, 53].

Values of E_0° adopted for this paper should not be expected to agree exactly with previously published values of E_0° , even though they are based on the same heats of formation at 298.16°K, as the values of E_0° involve also values of $H^\circ - E_0^\circ$, and the effects of rounding off values are also present.

XIV. Equilibrium Constants

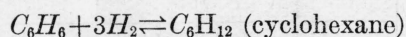
The equilibrium constants of the reactions listed in section I are given in tables 25 to 29 as functions of the temperature from 298.16° to 1,500°K. These equilibrium constants were derived from data in tables 1 to 26 of this paper and tables for the *n*-butenes in reference [4].

The equilibrium constants K_p are for pressures expressed in atmospheres, as the pressure chosen for the specification of the standard state is 1 atmosphere.

$$\log_{10} K_p = -\Delta F^\circ / (2.3026RT),$$

where ΔF° is the difference between the sums of the free energies of the products and of the reactants of the reaction to which K_p applies, the free energies being those of pure substances in the ideal gaseous state at 1 atmosphere pressure and at temperature T° K. The values of K_p in tables 25 to 29 are therefore calculated for reactions in the ideal gaseous state and differ from equilibrium constants for actual real gas conditions by amounts determined by the departure of real gas mixtures from ideal gas behavior.

Some reactions for which the equilibrium constants are given in tables 25 to 29 are discussed in the following paragraphs.



The equilibrium constants for the hydrogenation of benzene to cyclohexane have been determined experimentally by Burrows and Lucarini [54] and by Zharkova and Frost [55]. Their experimentally determined constants are compared in table 30 with the calculated constants derived from the free energy data of this paper.

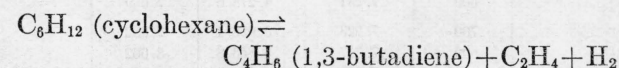
The equilibrium constant (table 25) varies rapidly with temperature. At ordinary temperatures, mixtures of benzene and hydrogen are very much less stable thermodynamically than cyclo-

TABLE 25.—Equilibrium constants K_p (pressures in atmospheres) for the reactions:

- (1) $C_6H_6(g) + 3H_2 \rightleftharpoons C_6H_{12}$ (cyclohexane, g).
- (2) C_6H_{12} (cyclohexane, g) \rightleftharpoons C_4H_6 (1,3-butadiene) + C_2H_4 + H_2 .
- (3) C_6H_{12} (cyclohexane, g) \rightleftharpoons C_4H_6 (1,3-butadiene) + C_2H_6 .

<i>T</i>	K_p (1)	K_p (2)	K_p (3)
$^\circ K$	atm ⁻³	atm ²	atm
298.16	1.43×10^{17}	8.32×10^{-34}	4.15×10^{-16}
300.00	8.53×10^{16}	1.69×10^{-33}	6.04×10^{-16}
400	7.06×10^7	6.61×10^{-21}	2.34×10^{-9}
500	1.85×10^2	2.94×10^{-12}	2.35×10^{-5}
600	3.05×10^{-2}	4.12×10^{-8}	1.12×10^{-2}
700	5.66×10^{-5}	1.95×10^{-4}	0.916
800	4.94×10^{-7}	0.113	24.5
900	1.23×10^{-8}	15.7	3.10×10^2
1,000	6.49×10^{-10}	8.03×10^3	2.30×10^5
1,100	5.89×10^{-11}	1.97×10^4	1.16×10^6
1,200	8.09×10^{-12}	2.79×10^5	4.40×10^6
1,300	1.53×10^{-12}	2.56×10^6	1.33×10^7
1,400	3.75×10^{-13}	1.69×10^7	3.40×10^8
1,500	1.11×10^{-13}	8.61×10^7	7.55×10^9

hexane, whereas at high temperatures of the order of 1,000° K, cyclohexane is very much less stable. Because of the rapid variation of K_p with temperature, experimental determinations of the equilibrium constant have been limited practically to a fifty degree range of temperatures from about 500° to 550° K. Considering this rapid variation, the agreement of the experimental and calculated equilibrium constants in table 30 is considered satisfactory.



In the thermal cracking of cyclohexane for commercial production of butadiene, cyclohexane is passed through a tube into which superheated steam at a high temperature (about 1,300° K) is injected to raise the temperature of the cyclo-

TABLE 26.—Equilibrium constants K_p (pressures in atmospheres) for the reactions:

- (1) $C_6H_{12}(\text{cyclohexane, g}) \rightleftharpoons C_4H_6(1,3\text{-butadiene}) + C_2H_2 + 2H_2$.
- (2) $C_6H_{12}(\text{cyclohexane, g}) \rightleftharpoons \frac{3}{2}C_4H_6(1,3\text{-butadiene}) + \frac{3}{2}H_2$.
- (3) $C_6H_{12}(\text{cyclohexane, g}) \rightleftharpoons 3C_2H_4$.
- (4) $2C_2H_4 \rightleftharpoons C_4H_6(1,3\text{-butadiene}) + H_2$.

T	$K_p(1)$	$K_p(2)$	$K_p(3)$	$K_p(4)$
$^{\circ}K$	atm^3	atm^3	atm^3	atm^0
298.16	1.61×10^{-58}	3.24×10^{-23}	5.50×10^{-21}	1.51×10^{-3}
300.00	5.20×10^{-58}	6.64×10^{-23}	1.10×10^{-20}	1.54×10^{-3}
400	8.83×10^{-38}	3.93×10^{-22}	1.88×10^{-18}	3.52×10^{-3}
500	1.78×10^{-28}	2.40×10^{-14}	4.40×10^{-11}	6.68×10^{-3}
600	2.95×10^{-17}	4.26×10^{-9}	3.86×10^{-6}	1.07×10^{-2}
700	2.99×10^{-11}	2.54×10^{-8}	1.14×10^{-2}	1.70×10^{-2}
800	8.83×10^{-7}	1.75×10^{-2}	4.67	2.42×10^{-2}
900	2.66×10^{-3}	2.84	4.83×10^2	3.26×10^{-2}
1,000	1.59	1.64×10^2	1.91×10^4	4.20×10^{-3}
1,100	2.94×10^2	4.52×10^2	3.76×10^4	5.25×10^{-2}
1,200	2.23×10^4	7.01×10^4	4.40×10^6	6.34×10^{-2}
1,300	8.53×10^5	7.05×10^5	3.40×10^7	7.53×10^{-2}
1,400	1.90×10^7	5.01×10^6	1.94×10^8	8.73×10^{-2}
1,500	2.76×10^8	2.72×10^7	8.67×10^8	9.93×10^{-2}

TABLE 27.—Equilibrium constant K_p (atm^{-1}), for the reaction $2C_2H_4 \rightleftharpoons n-C_4H_8$ (1-butene, *cis* and *trans*-2-butene and the equilibrium mixture of the *n*-butenes)

T	$K_p(atm^{-1})$	$K_p(atm^{-1})$	$K_p(atm^{-1})$	$K_p(atm^{-1})$
	1-butene	<i>cis</i> -2-butene	<i>trans</i> -2-butene	equilibrium mixture
$^{\circ}K$				<i>n</i> -butenes
298.16	1.38×10^{11}	1.27×10^{12}	4.67×10^{12}	6.08×10^{12}
300.00	1.07×10^{11}	9.70×10^{11}	3.52×10^{12}	4.59×10^{12}
400	3.40×10^6	1.48×10^7	3.60×10^7	5.42×10^7
500	6.84×10^3	1.85×10^4	3.63×10^4	6.16×10^4
600	1.06×10^2	2.01×10^3	3.51×10^3	6.58×10^3
700	5.86	8.57	1.39×10	2.83×10
800	6.55×10^{-1}	7.80×10^{-1}	1.21	2.64
900	1.20×10^{-1}	1.21×10^{-1}	1.81×10^{-1}	4.22×10^{-1}
1,000	3.11×10^{-2}	2.74×10^{-2}	4.00×10^{-2}	9.85×10^{-2}
1,100	1.04×10^{-2}	8.20×10^{-3}	1.18×10^{-2}	3.04×10^{-2}
1,200	4.17×10^{-3}	3.01×10^{-3}	4.26×10^{-3}	1.14×10^{-2}
1,300	1.95×10^{-3}	1.30×10^{-3}	1.82×10^{-3}	5.07×10^{-3}
1,400	1.02×10^{-3}	6.32×10^{-4}	8.85×10^{-4}	2.54×10^{-3}
1,500	5.82×10^{-4}	3.40×10^{-4}	4.69×10^{-4}	1.39×10^{-3}

TABLE 28.—Equilibrium constants K_p (pressures in atmospheres) for the reactions:

- (1) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$.
- (2) $2C_2H_5OH \rightleftharpoons C_4H_6(1,3\text{-butadiene}) + 2H_2O + H_2$.
- (3) $C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$.
- (4) $C_2H_4 + C_2H_2 \rightleftharpoons C_4H_6(1,3\text{-butadiene})$.

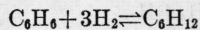
T	$K_p(1)$	$K_p(2)$	$K_p(3)$	$K_p(4)$
$^{\circ}K$	atm	atm^2	atm^{-1}	atm^{-1}
298.16	2.00×10^{-18}	5.43×10^{-5}	1.66×10	7.78×10^{21}
300.00	2.80×10^{-18}	6.97×10^{-5}	1.49×10	5.13×10^{21}
400	2.82×10^{-12}	1.57×10^{-1}	1.49×10^{-1}	2.64×10^{14}
500	1.25×10^{-8}	7.46×10	9.47×10^{-3}	1.10×10^{10}
600	3.68×10^{-6}	4.90×10^3	1.51×10^{-3}	1.30×10^7
700	2.12×10^{-4}	1.00×10^5	4.13×10^4	1.10×10^5
800	4.60×10^{-3}	9.66×10^5	1.58×10^{-4}	3.08×10^3
900	5.08×10^{-2}	5.66×10^6	7.59×10^{-5}	1.93×10^2
1,000	0.349	2.31×10^7	4.27×10^{-5}	21.2
1,100	1.70	7.28×10^7	2.68×10^{-5}	3.53
1,200	6.34	1.85×10^8	1.85×10^{-5}	0.792
1,300	19.2	4.08×10^8	1.36×10^{-5}	0.226
1,400	49.9	7.92×10^8	1.04×10^{-5}	7.78×10^{-2}
1,500	114.0	1.40×10^9	0.84×10^{-5}	3.10×10^{-2}

TABLE 29.—Equilibrium constants K_p (pressures in atmospheres) for the reactions:

- (1) $C_2H_4 \rightleftharpoons C_2H_2 + H_2$.
- (2) $C_2H_6 \rightleftharpoons C_2H_2 + 2H_2$.
- (3) $C_2H_4 + C_4H_6(1,3\text{-butadiene}) \rightleftharpoons C_6H_6(g) + 2H_2$.
- (4) $2C_4H_6(1,3\text{-butadiene}) \rightleftharpoons C_6H_6(g) + C_2H_4 + H_2$.

T	$K_p(1)$	$K_p(2)$	$K_p(3)$	$K_p(4)$
$^{\circ}K$	atm	atm^2	atm	atm
298.16	1.94×10^{-25}	3.88×10^{-43}	8.41×10^{15}	5.57×10^{18}
300.00	3.00×10^{-25}	8.41×10^{-43}	6.92×10^{15}	4.49×10^{18}
400	1.34×10^{-17}	3.77×10^{-29}	2.14×10^{12}	6.08×10^{14}
500	6.08×10^{-13}	7.60×10^{-21}	1.84×10^{10}	2.75×10^{12}
600	8.22×10^{-10}	3.03×10^{-15}	7.96×10^8	7.46×10^{10}
700	1.54×10^{-7}	3.27×10^{-11}	9.08×10^7	5.35×10^9
800	7.84×10^{-6}	3.61×10^{-8}	1.79×10^7	7.43×10^8
900	1.69×10^{-4}	8.59×10^{-6}	5.15×10^6	1.58×10^8
1,000	1.98×10^{-3}	6.92×10^{-4}	1.92×10^6	4.57×10^7
1,100	1.49×10^{-2}	2.53×10^{-2}	8.61×10^5	1.64×10^7
1,200	8.00×10^{-2}	0.507	4.44×10^5	7.00×10^6
1,300	0.333	6.40	2.54×10^5	3.37×10^6
1,400	1.12	56.0	1.57×10^5	1.80×10^6
1,500	3.21	290.0	1.04×10^5	1.05×10^6

TABLE 30.—A comparison of calculated and experimental values for the equilibrium constant K_p for the reaction:

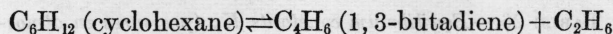


T	K_p (calculated)	K_p (experimental)	Observers *
$^{\circ}K$	atm^{-3}	atm^{-3}	
503.1	134.0	135.0	(55)
503.3	132.0	104.0	(55)
503.5	129.0	77.0	(55)
522.6	19.5	11.0	(55)
522.6	19.5	10.7	(55)
523.1	18.6	12.6	(55)
523.4	18.1	11.7	(55)
523.4	18.1	16.0	(55)
523.6	17.8	15.4	(55)
540.0	3.92	5.10	(54)
540.0	3.92	5.49	(54)
540.0	3.92	5.40	(54)
540.0	3.92	5.51	(54)
548.1	1.91	1.61	(55)
548.1	1.91	1.56	(55)
548.6	1.84	1.18	(55)
549.6	1.68	1.11	(55)
553.2	1.23	1.52	(54)
553.2	1.23	1.60	(54)
553.2	1.23	1.63	(54)

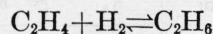
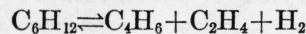
* (54) G. H. Burrows and C. Lucarini, (55) Z. R. Zharkova and A. V. Frost.

hexane from about 900° to 1,000° K. Under these conditions it is probable that the above reaction is one of the principal primary reactions taking place.

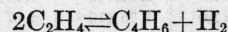
As will be seen from table 26 the square of the concentration of C_2H_4 in thermodynamic equilibrium with butadiene at 1,000° K is about 24 times the product of the concentrations of C_4H_6 and H_2 . For the same concentration of H_2 and C_4H_6 this means that the concentration of C_2H_4 is about 5 times that of butadiene. Schneider and Frolich [56] have shown that butadiene and hydrogen are the principal initial products resulting from the pyrolysis of ethylene, from which it would be inferred that the rate of cracking of butadiene to form ethylene must be appreciable. Hence in the production of butadiene from cyclohexane, the temperature of a cracked cyclohexane product high in butadiene should be lowered in a reasonably short time. As in the cracking reaction of cyclohexane, butadiene, and ethylene are formed in equal concentrations the establishment of thermodynamic equilibrium between C_2H_4 , C_4H_6 , and H_2 decreases the yield of butadiene.



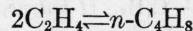
Ethane is not formed to any appreciable extent as a primary product in the thermal cracking of cyclohexane. The equilibrium indicated by the equation heading this subsection is probably the result of the two reactions:



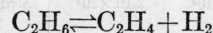
With increase of pressure on the gaseous system the concentration of ethane will increase relative to the concentration of ethylene in accordance with the law of mass action.



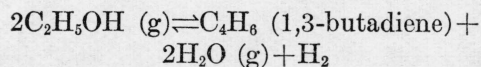
In the pyrolysis of ethylene at 725° C (1,000° K) Schneider and Frolich [56] found that 72 per cent of the product initially formed is C_4H_6 and H_2 . According to these authors the rate of the reaction is first order or less, indicating an intermediate reaction, possibly that of formation of an excited ethylene molecule or a free vinyl radical.



Schneider and Frolich [61] observed that butenes are initial products in the pyrolysis of C_2H_4 . In table 27 are given the equilibrium constants for the separate reactions forming 1-butene, *cis*-2-butene, *trans*-2-butene and an equilibrium mixture of *n*-butenes. The thermodynamic data on the butenes used in the calculation of these equilibrium constants were taken from reference [4].

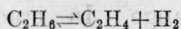


Experimental determinations of the equilibrium constant K_p for this reaction have been made by Kistiakowsky [57], Frey and Huppke [58], Viden-ski and Vinikova [59], Travers and Pearce [60], Pease and Durgan [61], and Travers and Hockin [62]. In table 31 their results are compared with calculated values interpolated from table 28.



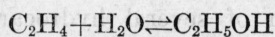
In the Lebedev process for making butadiene, ethyl alcohol is passed over a mixed dehydrogenation-dehydration catalyst at a temperature of about 700° K. The over-all reaction of the process is as written above. It is likely, however, that intermediate reactions are involved.

TABLE 31.—A comparison of calculated and experimental values for the equilibrium constant K_p for the reaction:

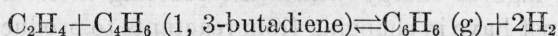


K	K_p (calculated)	K_p (experimental)	Observers ^a
$^{\circ}\text{K}$	<i>atm</i>	<i>atm</i>	
653	3.68×10^{-5}	4.04×10^{-5}	(57)
673	7.98×10^{-5}	8.2×10^{-5}	(58)
723	4.63×10^{-4}	5.16×10^{-4}	(57)
		5.6×10^{-4}	(58)
773	2.16×10^{-3}	3.2×10^{-3}	(59)
		2.4×10^{-3}	(58)
823	8.41×10^{-3}	7.4×10^{-3}	(60)
843	0.0139	0.0153	(60)
863	.0223	.0244	(60)
		.0245	(61)
873	.0281	.031	(61)
883	.0351	.0359	(60)
		.033	(62)
893	.0438	.0446	(60)
903	.0542	.054	(60)
923	.0822	.082	(61)
		.078	(60)
973	.216	.20	(61)

^a (57) G. B. Kistiakowsky, (58) F. E. Frey and W. F. Huppke, recalculated, G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, (59) A. A. Videnski and S. G. Vinikova, (60) M. W. Travers and T. J. P. Pearce, (61) R. N. Pease and E. S. Durgan, (62) M. W. Travers and L. E. Hockin.

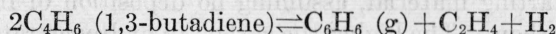


Experimental determinations of K_p for this reaction have been made by Stanley, Youell and Dymock [63], Appleby, Glass, and Horsley [64], and Bliss and Dodge [65]. The experimental values of K_p are compared with calculated values in table 32.



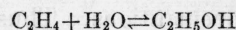
Schneider and Frolich [56] found that benzene was the most abundant single initial product resulting from the pyrolysis of a mixture of ethylene (90 percent) and butadiene (10 percent) at 1,000° K and one-fifth of an atmosphere. It is probable that there is an intermediate metastable

complex formed by C_2H_4 and C_4H_6 , possibly the triolefin C_6H_8 , which breaks down, giving C_6H_6 .



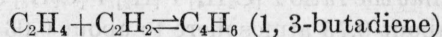
Schneider and Frolich [56] suggest that benzene may be formed as a result of a coalescence of two butadiene molecules.

TABLE 32.—A comparison of calculated and experimental values for the equilibrium constant K_p of the reaction:



T	K_p (calculated)	K_p (experimental)	Observers ^a
$^{\circ}\text{K}$	<i>atm⁻¹</i>	<i>atm⁻¹</i>	
418	8.28×10^{-2}	6.8×10^{-2}	(68)
448	3.42×10^{-2}	3.6×10^{-2}	(68)
		2.93×10^{-2}	(69)
473	1.78×10^{-2}	1.65×10^{-2}	(68)
		1.72×10^{-2}	(69)
498	0.989×10^{-2}	1.07×10^{-2}	(68)
		0.984×10^{-2}	(69)
523	5.83×10^{-3}	6.7×10^{-3}	(68)
		6.28×10^{-3}	(69)
548	3.61×10^{-3}	3.83×10^{-3}	(69)
593	1.68×10^{-3}	1.87×10^{-3}	(70)
623	1.07×10^{-3}	1.49×10^{-3}	(70)
651	$.736 \times 10^{-3}$	1.26×10^{-3}	(70)

^a (63) H. M. Stanley, J. E. Youell, J. B. Dymock, (64) M. P. Appleby, J. V. S. Glass, G. F. Horsley, (65) R. H. Bliss, B. F. Dodge.



The reaction forming butadiene from ethylene and acetylene in equimolar proportion was reported in 1866 by Berthelot [66] and has been studied recently by Naragon, Burk, and Lankelma [67], who conclude that acetylene in the absence of catalysts reacts more readily with ethylene than ethylene does with itself. As acetylene is so reactive, other reactions also occur, leading to products of higher molecular weight. Considering that the equilibrium constant for the formation of butadiene from ethylene and acetylene is very favorable at low and moderate temperatures, a catalyst specific for this reaction is desirable [68].

XV. Comments on Cracking Reactions

The law of mass action and tables of equilibrium constants for different temperatures are helpful in the analysis of data on the products of cracking and condensation reactions of hydrocarbons. Thus tables of equilibrium constants show how, with increase of temperature, the equilibrium concentrations of unsaturated hydrocarbons increase with

respect to the saturated hydrocarbons. The law of mass action determines the expected rate of increase in the relative equilibrium concentration of saturated hydrocarbons with increase of pressure. Besides depending upon temperature and pressure, the relative equilibrium concentrations of saturated and unsaturated hydrocarbons formed

by cracking and condensation reactions are dependent upon the carbon to hydrogen ratio of the starting material, assuming no deposition of free carbon. The higher the carbon to hydrogen ratio, the greater the relative equilibrium concentration of the unsaturated hydrocarbons.

Two investigations of the products of the thermal cracking of hexane, one at high [69] and the other at low pressure [70], illustrate in a striking manner the influence of changes of pressure upon equilibrium concentrations. Thus at a pressure of 1,000 atmospheres and at temperatures of 783° K, there was no measurable concentration of hydrogen or any unsaturated hydrocarbon, whereas at a pressure of 0.18 atmosphere and 698° K the concentration of the unsaturated hydrocarbons exceeded that of the saturated compounds. In low pressure cracking reactions, equilibrium is approached from the side of low concentration of unsaturates, and in high pressure cracking from the side of high concentration of unsaturates.

The establishment of approximate equilibrium concentrations of hydrocarbons at temperatures of 700° to 800° K in the absence of catalysts requires times of the order of several hours. Thus in the products of a cracking process at high pressures [69] involving several reactions, one finds that the ratio $P[C_2H_4] \cdot P[H_2] / P[C_2H_6]$ changes from about 0.75 atmosphere to about 0.03 atmosphere during a period of about 2 hours at temperatures of 730° K. The equilibrium value is about 10^{-3} atmosphere. When several reactions occur in succession, the slowest reaction controls the approach to final equilibrium. For the most rapid reaction the apparent equilibrium constant as calculated from experimental compositions approaches the theoretical value relatively soon

even though general equilibrium is not yet attained, so that the individual compositions continue to change. In cracking gas oil at 1,223° K [71] and 0.23 atmosphere, the proportions of C_4H_6 , H_2 , and C_2H_4 after a "contact time" of 0.05 second are fairly consistent with the equilibrium constant for the reaction $2C_2H_4 \rightleftharpoons C_4H_6 + H_2$ as given in table 27, whereas the proportions of butanes, butenes, butadiene, ethylene, ethane, and hydrogen were not yet in approximate agreement with equilibrium constants for simple dehydrogenation reactions. On the other hand, the compositions obtained in the cracking of isobutane [72], probably at about atmospheric pressure, near 873° K and 923° K indicate values of $P[C_4H_6] \cdot P[H_2] / P^2[C_2H_4]$ that differ from the calculated values of the equilibrium constant by factors of the order of 100 after contact times of the order of a minute and of several seconds, respectively. In both cases these experimental values were changing with time. The well-known strong dependence of reaction rate on temperature is particularly evident in this case. The rates of many of these reactions double for each 15 to 25 degrees centigrade rise in temperature. Correlations of data for reaction rates for the thermal decomposition of several hydrocarbons will be found in a review paper by Steacie [73] and a discussion of the prediction of reaction rates is given in a paper by Daniels [74]. Numerous papers by Eyring and co-authors treat the subject of reaction rates, considering details of the structure of the activated complex, the configuration of highest energy which the reacting molecules must have in changing from reactants to products of a reaction [75].

XVI. References

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