U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1634

Part of Journal of Research of the National Bureau of Standards, Volume 34, February 1945

HEATS, FREE ENERGIES, AND EQUILIBRIUM CONSTANTS OF SOME REACTIONS INVOLVING O_2, H_2, H_2O, C, CO, CO_2, AND CH_4[1]

By Donald D. Wagman, John E. Kilpatrick,[2] William J. Taylor,[2] Kenneth S. Pitzer,[3] and Frederick D. Rossini

ABSTRACT

Values are presented for the following thermodynamic properties: The heat-content function, $(H^\circ - H_0^\circ)/T$, the free-energy function, $(F^\circ - H_0^\circ)/T$, the entropy, S°, the heat content, $H^\circ - H_0^\circ$, and the heat capacity, C_p°, for O_2 (gas) to 5,000 °K, H_2 (gas) to 5,000 °K, H_2O (gas) to 3,000 °K, N_2 (gas) to 5,000 °K, C (solid, graphite) to 1,500 °K, C (solid, diamond) to 1,200 °K, CO (gas) to 5,000 °K, CO_2 (gas) to 3,500 °K, and CH_4 (gas) to 1,500 °K; the standard entropy, S°, for H_2O (liq) at 25 °C; the heat of formation, ΔHf°, the free energy of formation, ΔFf°, and the equilibrium constant of formation, Kf, from the elements, for H_2O (liq) at 25 °C, and for H_2O (gas), CO (gas), CO_2 (gas), and CH_4 (gas), to 1,500 °K; the increment in heat content, ΔH°, and the increment in free energy, ΔF°, for the transition of graphite into diamond, to 1,200 °K and to 20,000 atmospheres.

From the foregoing, values were calculated for the increment in heat content, ΔH°, the increment in free energy, ΔF°, and the equilibrium constant, K, for the following reactions, most of which are important in connection with the production of liquid hydrocarbon fuels from natural gas or coal and hydrogen:

C(solid, graphite) + CO_2(gas) = 2CO (gas).
C(solid, graphite) + H_2O (gas) = CO(gas) + H_2(gas).
CO(gas) + 1/2O_2(gas) = CO_2(gas).
CO(gas) + H_2O (gas) = CO_2(gas) + H_2(gas).
CH_4(gas) + 1/2O_2(gas) = CO(gas) + 2H_2(gas).
CH_4 (gas) + CO_2(gas) = 2CO(gas) + 2H_2(gas).
CH_4(gas) + H_2O(gas) = CO(gas) + 3H_2(gas).
CH_4(gas) + 2H_2O(gas) = CO_2(gas) + 4H_2(gas).

A table of the fundamental constants used in the calculations is given.

CONTENTS

---

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

[3] Consultant to the American Petroleum Institute Research Project 44 at the National Bureau of Standards; Professor of Chemistry, University of California, Berkeley, Calif.

I. INTRODUCTION

In connection with the work of the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 at the National Bureau of Standards, values for thermodynamic properties of the simple substances oxygen, hydrogen, water, nitrogen, carbon, carbon monoxide, carbon dioxide, and methane have been recalculated. These data have been used to calculate the heats, free energies, and equilibrium constants of a number of reactions involved in the production of liquid hydrocarbon fuels from natural gas or coal and hydrogen. The results of these calculations are presented in this report.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, CONSTANTS, ETC.

The unit of energy used in this paper is the conventional thermochemical calorie, defined as follows [1]:[4]

$$1 \text{ calorie} = 4.1833 \text{ international joules (NBS)}. \qquad (1)$$

The unit of pressure is the conventional standard atmosphere, defined as follows [2, 7]:

$$1 \text{ atmosphere} = 1{,}013{,}250 \text{ dynes/cm}^2. \qquad (2)$$

The constants in eq 1 and 2 are conventional constants, and are not subject to experimental error.

The molecular weights were calculated from the values given in the 1941 table of International Atomic Weights [3].

The value of the PV product for an ideal gas (a real gas at zero pressure) at 0°C, $(PV)^{P=0}_{0^\circ C}$, which is equal to the product of the gas constant per mole and the absolute temperature of the ice point, $(RT)_{0^\circ C}$, is taken from the value calculated by Cragoe [4]:

$$(PV)^{P=0}_{0^\circ C} = (RT)_{0^\circ C} = 2271.16 \text{ absolute joules/mole}. \qquad (3)$$

The uncertainty in the foregoing relation is estimated to be ±0.002 percent.

The relation between the absolute watt and the international watt (NBS) is taken from the value recommended by Crittenden and Curtis [5]:

$$1 \text{ international watt (NBS)} = 1.00017 \text{ absolute watts}. \qquad (4)$$

The uncertainty in the foregoing relation is estimated to be ±0.005 percent.

---

[4] Figures in brackets indicate the literature references at the end of the paper.

The additional constants used in the present calculations are (1) the absolute temperature of the ice point, $T_{0^\circ\text{C}}$; (2) the velocity of light, *c;* (3) the Avogadro number (chemical scale) *N;* and (4) the Planck constant, *h*. The relation between the liter and the cubic centimeter has been utilized to convert several quantities to pressure-volume units, since they are often useful. The values recommended by Birge [6] for these constants have been used.

The foregoing values of the constants lead to the consistent set of fundamental and derived constants that are given in table 1. The uncertainties of the constants have been reestimated in some cases by the present authors.

The values of the constants in table 1 have been used to calculate the constants in the equations for the contributions of translation and of rotation of a rigid molecule to the several thermodynamic functions. The contribution of translation is given by the Sackur-Tetrode equation, and is exact for all molecules. The contribution of a rigid rotator is a useful approximation to the rotational contribution in actual molecules. See references [8, 9].

TABLE 1.—*Values of the constants*

No.	Relation	From
a	1 liter $=1000.028 \pm 0.004$ cm^3	[6]
b	1 atm $=1{,}013{,}250$ dyne/cm^2	Definition, [2]
c	1 int. joule (NBS) $=1.00017 \pm 0.00005$ abs. joule	[5]
d	1 cal $=4.1833$ int. joule (NBS)	Definition, [1]
e	$=4.18401 \pm 0.00021$ abs. joule	d, c
f	$=41.2930 \pm 0.0021$ cm^3 atm	d, c, b
g	$=0.0412918 \pm 0.0000021$ liter atm	d, c, b, a
h	$(PV)_{0^\circ\text{C}}^{P=0}=(RT)_{0^\circ\text{C}}=2271.16 \pm 0.04$ abs. joule/mole	[4]
i	$=22414.6 \pm 0.4$ cm^3 atm/mole	h, b
j	$=22.4140 \pm 0.0004$ liter atm/mole	h, b, a
k	$T_{0^\circ\text{C}}=273.160 \pm 0.010$ °K	[6]
l	$R=(RT)_{0^\circ\text{C}}/T_{0^\circ\text{C}}=8.31439 \pm 0.00034$ abs. joule/deg mole	h, k
m	$=8.31298 \pm 0.00054$ int. joule/deg mole	l, c
n	$=1.98718 \pm 0.00013$ cal/deg mole	l, e
o	$=82.0567 \pm 0.0034$ cm^3 atm/deg mole	l, b
p	$=0.0820544 \pm 0.0000034$ liter atm/deg mole	l, b, a
q	$N=(6.02283 \pm 0.0022) \times 10^{23}$/mole	[6]
r	$k=(R/N)=(1.38048 \pm 0.00050) \times 10^{-16}$ erg/deg	l, q
s	$h=(6.6242 \pm 0.0044) \times 10^{-27}$ erg sec	[6]
t	$c=(2.99776 \pm 0.00008) \times 10^{10}$ cm/sec	[6]
u	$Z=Nhc=11.9600 \pm 0.0036$ abs. joule cm/mole	q, s, t
v	$=11.9580 \pm 0.0036$ int. joule cm/mole	u, c
w	$=2.8585 \pm 0.0009$ cal cm/mole	u, e
x	$(Z/R)=(hc/k)=1.43847 \pm 0.00045$ cm deg	u, l

The equations in table 2 yield the values of the thermodynamic functions in units of calories, degrees, and moles. The logarithms are common logarithms, to the base 10. M is the molecular weight in grams, and T is the absolute temperature in degrees Kelvin. I is the value of the two equal moments of inertia, in g-cm^2, of a linear molecule about axes perpendicular to the axis of the molecule. I_1, I_2, and I_3, are the three principal moments of inertia, in g-cm^2, not necessarily unequal in value, of a nonlinear molecule. Separate equations are required for the rotational contributions of a diatomic or linear polyatomic molecule, and those of a nonlinear polyatomic molecule. The symmetry number, σ, is the number of ways the molecule may be superimposed upon itself by rotation of the entire molecule. For linear molecules the value of σ is either 1 or 2; the equations for the rotational free energy and entropy of a linear molecule are given explicitly for these two cases.

TABLE 2.—*Summary of equations, with constants, for calculating the values of the thermodynamic functions for translation (of all molecules) and rotation (of rigid molecules)*

[Units: $(H^\circ - H_0^\circ)/T$, C°, $(F^\circ - H_0^\circ)/T$, and S° in cal/deg mole; T in °K; M in g/mole; I, I_1, I_2, and I_3 in g-cm^2; σ, a dimensionless integer; logarithms to the base 10.]

TRANSLATION (OF ALL MOLECULES)

$(H^\circ - H_0^\circ)/T = C_p^\circ = 4.9680$
$(F^\circ - H_0^\circ)/T = -6.8635 \log M + 7.2820 - 11.4391 \log T$
$S^\circ = 6.8635 \log M - 2.3141 + 11.4391 \log T$

ROTATION (OF RIGID MOLECULES)

I. *Diatomic or linear polyatomic molecules.*
  $(H^\circ - H_0^\circ)/T = C^\circ = 1.9872$
  (a) σ (symmetry number) $= 1$:
    $(F^\circ - H_0^\circ)/T = -4.5757 \log (I \times 10^{39}) + 2.7676 - 4.5757 \log T$
    $S^\circ = 4.5757 \log (I \times 10^{39}) - 0.7804 + 4.5757 \log T$
  (b) σ (symmetry number) $= 2$:
    $(F^\circ - H_0^\circ)/T = -4.5757 \log (I \times 10^{39}) + 4.1450 - 4.5757 \log T$
    $>S^\circ = 4.5757 \log (I \times 10^{39}) - 2.1578 + 4.5757 \log T$
II. *Nonlinear polyatomic molecules.*
  $(H^\circ - H_0^\circ)/T = C^\circ = 2.9808$
  $(F^\circ - H_0^\circ)/T = -2.2878 \log (I_1 I_2 I_3 \times 10^{117}) + 4.5757 \log \sigma + 3.0140 - 6.8635 \log T$
  $S^\circ = 2.2878 \log (I_1 I_2 I_3 \times 10^{117}) - 4.5757 \log \sigma - 0.0332 + 6.8635 \log T$

III. HEAT-CONTENT FUNCTION, FREE-ENERGY FUNCTION, ENTROPY, HEAT CONTENT, AND HEAT CAPACITY

1. METHOD OF CALCULATION

Values of the thermodynamic properties of the simple molecules, O_2, H_2, H_2O, N_2, CO, and CO_2, in the ideal gaseous state and to high temperatures, were calculated statistically from spectroscopic and other molecular data by Johnston, et. al. [10, 11, 12, 13], Giauque, et. al. [14, 15, 16], Gordon [17, 18], and Kassel [19]. Since such new spectroscopic data as have become available would not lead to values of the thermodynamic functions significantly different than those obtained in the foregoing calculations, it was not considered necessary or justified to repeat these calculations in detail. The values required for the present investigation were obtained by converting the existing values to new ones based on the new values of the fundamental constants and the unit of energy.

The important corrections required to be made arise from the following: (a) Change in the value of the gas constant R from 1.9869 to 1.98718 cal/deg mole, the ratio being 1.00014; (b) change in the value of the constant of the Sackur-Tetrode equation for entropy of translation from -2.300 to -2.3141 cal/deg mole; (c) change in the value hc/k from 1.43242 to 1.43847 cm deg, the ratio being 1.004224; (d) changes in the atomic weights of hydrogen and carbon from 1.0078 to 1.0080 and from 12.00 to 12.010, respectively; (e) correction for rotational stretching in CO_2 and H_2O.

The foregoing corrections were handled in the following manner:

(a) Each thermodynamic function was increased in value by the factor 1.00014, the ratio of the new to the old value of the gas constant.

(b) A constant amount of $+0.014$ was subtracted from the value of the entropy for translation and added to the value of the free-energy function for translation, for each molecule.

(c) The values previously calculated for the rotational and vibrational contributions to a given thermodynamic property were taken to be correct for a new, slightly higher temperature T^*, such that $T^*/T = 1.004224$, the ratio of the new to the old value of hc/k. This procedure is possible because the previous calculations involved summations with the partition function, in which hc/k appears as a multiplier of $1/T$, as in the expression

$$Q=\sum_i p_i e^{-(hc/k)\,(\bar{\nu}_i/T)} \tag{5}$$

The tabulated functions were interpolated from the temperatures T^* to even temperatures, after subtraction of the temperature-dependent term of the Sackur-Tetrode equation for the translational contribution to the entropy and the free-energy function. On a plot of any function $f(T)$ against T, the temperature for which the calculation was originally made, the corrected value of $f(T)$ for the temperature T is the value of the function at $(1-1/1.004224)T=0.00421T$ degrees below T. In practice, the slope of the function at T was calculated by averaging $\Delta f(T)/\Delta T$ for the intervals above and below T. The correction to $f(T)$ due to the change in hc/k is then $-0.00421T\,df(T)/dT$. The correction varies slowly with the temperature.

(d) The entropy and the free-energy function were increased and decreased, respectively, by $3/2R\ln(1+\Delta M/M)$, where M is the molecular weight and ΔM the change in the molecular weight for the given substance. Since $\Delta M/M$ is very small, this expression reduces to $3/2R\Delta M/M$ or $2.98\Delta M/M$.

(e) A small additive correction for rotational stretching, as given by Wilson [20], was made to each of the thermodynamic functions of H_2O and CO_2.

The complete equations used for the conversion are as follows, with the old values primed:

$$(H^\circ-H_0^\circ)/T=1.00014\{[(H^\circ-H_0^\circ)/T]'-0.00421Td[(H^\circ-H_0^\circ)/T]'/dT\}. \tag{6}$$

$$(F^\circ-H_0^\circ)/T=1.00014\{[(F^\circ-H_0^\circ)/T]'-0.00421[Td[(F^\circ-H_0^\circ)/T]'/dT+5/2R']+0.014\}-2.98\Delta M/M. \tag{7}$$

$$S^\circ=1.00014\{(S^\circ)'-0.00421[Td(S^\circ)'/dT-5/2R']-0.014\}+2.98\Delta M/M. \tag{8}$$

$$C_p^\circ=1.00014\{(C_p^\circ)'-0.00421Td(C_p^\circ)'/dT\}. \tag{9}$$

In the case of methane, the statistical calculations made by one of the authors [21] were extended to include other temperatures.

In the case of carbon (graphite) and carbon (diamond), the existing calorimetric data were subjected to graphical analysis to yield selected "best" values for the heat-content function, free-energy function, entropy, heat content, and heat capacity, to 1,500° K for graphite and to 1,200° K for diamond.

2. DATA USED IN THE CALCULATIONS

The data used in the present calculations, according to the procedure described in the preceding section, were from the following sources:

O_2(*gas*).—Statistical calculations from Johnston and Walker [10, 11], who gave values for the free-energy function, the entropy, the heat content, and the heat capacity, to 5,000° K. See also Gordon and Barnes [22].

H_2 (*gas*).—Statistical calculations from Davis and Johnston [12], who gave values for the free-energy function, entropy, heat content, and heat capacity to 5,000° K, and from Giauque [14], who gave values for the free-energy function. See also Gordon and Barnes [23] and Libby [24].

H_2O (*gas*).—Statistical calculations from Gordon [17, 18], who gave values for the free-energy function, entropy, and heat capacity, to 3,000° K. See also Libby [24].

N_2 (*gas*).—Statistical calculations from Johnston and Davis [13], who gave values for the entropy, heat content, and heat capacity to 5,000° K, and from Giauque and Clayton [15], who gave values for the free-energy function to 5,000° K.

CO (*gas*).—Statistical calculations from Johnston and Davis [13], who gave values for the entropy, heat content, and heat capacity, to 5,000° K, and from Clayton and Giauque [16], who gave values for the free-energy function to 5,000° K. See also Gordon and Barnes [22], and Kassel [25].

CO_2 (*gas*).—Statistical calculations from Kassel [19], who gave values for the free-energy function, heat content, and heat capacity, to 3,500° K. See also Gordon [26] and Gordon and Barnes [23].

CH_4 (*gas*).—Statistical calculations from Pitzer [21], who gave values for the free-energy function, heat content, entropy, and heat capacity to 1,500° K.

C (*solid, graphite*).—Experimental data on heat capacity and heat content from Nernst [27] from 30° to 85° K, from Worthing [28] (indirect measurements) from 1,170° to 2,400° K, from Magnus [29] from 370° to 1,200° K, from Schläpfer and Debrunner [30] from 370° to 1,400° K, and from Jacobs and Parks [31] from 87° to 300° K. See also Magnus [32].

C (*solid, diamond*).—Experimental data on heat capacity and heat content from Weber [33, 34] from 283° to 600° K, from Magnus and Hodler [35] from 670° to 1,180° K, and from Pitzer [36] from 70° to 288° K. See also Bettendorf and Wüllner [37], Nernst and Lindemann [38], and Robertson, Fox, and Martin [39].

3. RESULTS FOR O_2, H_2, H_2O, N_2, C, CO, CO_2, AND CH_4

The resulting values of the thermodynamic properties for O_2 (gas), H_2 (gas), H_2O (gas), N_2 (gas), C (solid, graphite), C (solid, diamond), CO (gas), CO_2 (gas), and CH_4 (gas) are presented in tables 3, 4, 5, 6, and 7, which give, respectively, values of the heat-content function, $(H°-H°_0)/T$, the free-energy function, $(F°-H°_0)/T$; the entropy, $S°$, the heat content, $H°-H°_0$, and the heat capacity, $C_p°$.

A value for the entropy of liquid water at 25° C may be obtained from the value for gaseous water at 25° C and the standard entropy of vaporization of water, as given by eq 20:

$$H_2O(\text{liq.});\ S°_{298.16}=16.716 \pm 0.016 \text{ cal/deg mole.} \qquad (10)$$

TABLE 3.—*Values of the heat-content function,* $(H^\circ - H^\circ_0)/T$, *for* O_2 *(gas),* H_2 *(gas),* H_2O *(gas),* N_2 *(gas),* C *(solid, graphite),* C *(solid, diamond),* CO *(gas),* CO_2 *(gas), and* CH_4 *(gas)*

Compound	Formula	State	Temperature in degrees Kelvin													
			0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Heat-content function, $(H^\circ - H^\circ_0)/T$, in calories per degree mole													
Oxygen	O_2	Gas	0	------	------	6.9221	6.9307	6.9418	6.9424	6.9811	7.0484	7.1320	7.2248	7.3176	7.4107	7.4970
Hydrogen	H_2	do	0	------	------	------	6.7771	6.7877	6.7882	6.8275	6.8590	6.8810	6.9022	6.9218	6.9423	6.9658
Water	H_2O	do	0	------	------	------	------	7.934	7.933	7.975	8.039	8.122	8.222	8.333	8.452	8.580
Nitrogen	N_2	do	0	------	------	6.9465	6.9482	6.9502	6.9503	6.9559	6.9701	6.9967	7.0361	7.0857	7.1422	7.2025
Carbon (graphite)	C	Solid	0	0.1445	0.28770	0.45986	0.64987	0.84369	0.85101	1.2565	1.6416	1.9968	2.3171	2.6021	2.8549	3.0746
Carbon (diamond)	C	do	0	.01664	.05920	.14528	.27549	.4297	.4360	0.8125	1.204	1.583	1.936	2.255	2.538	2.782
Carbon monoxide	CO	Gas	0	------	------	6.9470	6.9495	6.9514	6.9515	6.9594	6.9799	7.0159	7.0654	7.1247	7.1895	7.2565
Carbon dioxide	CO_2	do	0	------	------	------	------	7.5064	7.5154	7.9870	8.4455	8.8707	9.2590	9.6117	9.9332	10.222
Methane	CH_4	do	0	------	------	------	------	8.039	8.042	8.307	8.730	9.249	9.816	10.401	10.985	11.56

Compound	Formula	State	1,100	1,200	1,250	1,300	1,400	1,500	1,750	2,000	2,500	3,000	3,500	4,000	4,500	5,000
			Heat-content function, $(H^\circ - H^\circ_0)/T$, in calories per degree mole													
Oxygen	O_2	Gas	7.5775	7.6533	7.6893	7.7238	7.7893	7.8509	7.9885	8.1094	8.3196	8.5000	8.6595	8.8038	8.9295	9.0440
Hydrogen	H_2	do	6.9927	7.0230	7.0387	7.0563	7.0919	7.1295	7.2307	7.3358	7.5402	7.7286	7.8963	8.0420	8.1733	8.2898
Water	H_2O	do	8.709	8.844	8.912	8.981	9.116	9.251	9.57	9.88	10.42	10.86	------	------	------	------
Nitrogen	N_2	do	7.2650	7.3273	7.3580	7.3882	7.4467	7.5024	7.6327	7.7497	7.9356	8.0816	8.1986	8.2944	8.3756	8.4405
Carbon (graphite)	C	Solid	3.269	3.442	3.522	3.600	3.744	3.876	------	------	------	------	------	------	------	------
Carbon (diamond)	C	do	2.990	3.168	------	------	------	------	------	------	------	------	------	------	------	------
Carbon monoxide	CO	Gas	7.3238	7.3898	7.4221	7.4538	7.5149	7.5725	7.7033	7.8182	8.0028	8.1448	8.2572	8.3487	8.4238	8.4905
Carbon dioxide	CO_2	do	10.487	10.727	10.841	10.949	11.151	11.336	11.74	12.07	12.59	12.98	13.29	------	------	------
Methane	CH_4	do	12.11	12.65	12.90	13.15	13.63	14.09	------	------	------	------	------	------	------	------

TABLE 4.—*Values of the free-energy function* $(F^\circ - H_0^\circ)/T$, *for* O_2 *(gas)*, H_2 *(gas)*, H_2O *(gas)*, N_2 *(gas)*, C *(solid, graphite)*, C *(solid, diamond)*, CO *(gas)*, CO_2 *(gas)*, *and* CH_4 *(gas)*

Compound	Formula	State	Temperature, in degrees Kelvin													
			0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Free-energy function, $(F^\circ - H_0^\circ)/T$, in calories per degree mole													
Oxygen	O_2	Gas	0	--------	--------	-39.297	-40.835	-42.061	-42.106	-44.112	-45.675	-46.968	-48.071	-49.044	-49.911	-50.697
Hydrogen	H_2	do	0	--------	--------	--------	-23.331	-24.423	-24.465	-26.422	-27.950	-29.203	-30.265	-31.186	-32.004	-32.738
Water	H_2O	do	0	--------	--------	--------	--------	-37.172	-37.221	-39.508	-41.295	-42.768	-44.026	-45.131	-46.120	-47.018
Nitrogen	N_2	do	0	--------	--------	-36.044	-37.595	-38.817	-38.859	-40.861	-42.415	-43.688	-44.769	-45.711	-46.550	-47.306
Carbon (graphite)	C	Solid	0	-0.0739	-0.1582	-0.2639	-0.3866	-0.5172	-0.5227	-0.8245	-1.146	-1.477	-1.810	-2.138	-2.459	-2.771
Carbon (diamond)	C	do	0	-0.0055	-0.0186	-0.0462	-0.0919	-0.1532	-0.1558	-0.331	-0.554	-0.808	-1.078	-1.358	-1.640	-1.920
Carbon monoxide	CO	Gas	0	--------	--------	-37.574	-39.124	-40.350	-40.391	-42.393	-43.947	-45.222	-46.308	-47.254	-48.097	-48.860
Carbon dioxide	CO_2	do	0	--------	--------	--------	--------	-43.555	-43.601	-45.828	-47.667	-49.238	-50.636	-51.895	-53.047	-54.109
Methane	CH_4	do	0	--------	--------	--------	--------	-36.46	-36.51	-38.86	-40.75	-42.39	-43.86	-45.21	-46.47	-47.65

Compound	Formula	State	1,100	1,200	1,250	1,300	1,400	1,500	1,750	2,000	2,500	3,000	3,500	4,000	4,500	5,000
			Free-energy function, $(F^\circ - H_0^\circ)/T$, in calories per degree mole													
Oxygen	O_2	Gas	-51.415	-52.077	-52.390	-52.695	-53.272	-53.808	-55.027	-56.103	-57.930	-59.468	-60.798	-61.958	-62.990	-63.947
Hydrogen	H_2	do	-33.402	-34.012	-34.305	-34.576	-35.098	-35.590	-36.696	-37.669	-39.328	-40.719	-41.922	-42.988	-43.942	-44.809
Water	H_2O	do	-47.842	-48.605	-48.968	-49.318	-49.989	-50.622	-52.08	-53.38	-55.65	-57.59	--------	--------	--------	--------
Nitrogen	N_2	do	-47.994	-48.629	-48.929	-49.218	-49.768	-50.284	-52.449	-52.478	-54.228	-55.687	-56.941	-58.043	-59.025	-59.910
Carbon (graphite)	C	Solid	-3.073	-3.365	-3.509	-3.647	-3.919	-4.181	--------	--------	--------	--------	--------	--------	--------	--------
Carbon (diamond)	C	do	-2.195	-2.46	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
Carbon monoxide	CO	Gas	-49.554	-50.196	-50.497	-50.789	-51.345	-51.884	-53.041	-54.078	-55.842	-57.314	-58.578	-59.688	-60.676	-61.566
Carbon dioxide	CO_2	do	-55.096	-56.019	-56.460	-56.887	-57.706	-58.461	-60.26	-61.85	-64.60	-67.11	-68.98	--------	--------	--------
Methane	CH_4	do	-48.78	-49.86	-50.38	-50.89	-51.88	-52.84	--------	--------	--------	--------	--------	--------	--------	--------

TABLE 5.—*Values of the entropy, $S°$, for O_2 (gas), H_2 (gas), H_2O (gas), N_2 (gas), C (solid, graphite), C (solid, diamond), CO (gas), CO_2 (gas), and CH_4 (gas)*

Compound	Formula	State	Temperature in degrees Kelvin													
			0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Entropy, $S°$, calories per degree mole													
Oxygen	O_2	Gas	0	--------	--------	46.219	47.766	49.003	49.048	51.093	52.723	54.100	55.296	56.362	57.322	58.194
Hydrogen	H_2	do	0	--------	--------	--------	30.108	31.211	31.253	33.250	34.809	36.084	37.167	38.108	38.946	39.704
Water	H_2O	do	0	--------	--------	--------	--------	45.106	45.154	47.483	49.334	50.890	52.248	53.464	54.572	55.598
Nitrogen	N_2	do	0	--------	--------	42.990	44.543	45.767	45.809	47.818	49.385	50.685	51.805	52.797	53.692	54.509
Carbon (graphite)	C	Solid	0	0.2184	0.4459	0.7238	1.0365	1.3609	1.3737	2.081	2.788	3.474	4.127	4.740	5.314	5.846
Carbon (diamond)	C	do	0	0.0221	0.0778	0.1915	0.3674	0.5829	0.5918	1.14	1.76	2.39	3.01	3.61	4.18	4.70
Carbon monoxide	CO	Gas	0	--------	--------	44.521	46.074	47.301	47.342	49.352	50.927	52.238	53.373	54.379	55.287	56.116
Carbon dioxide	CO_2	do	0	--------	--------	--------	--------	51.061	51.116	53.815	56.113	58.109	59.895	61.507	62.980	64.331
Methane	CH_4	do	0	--------	--------	--------	--------	44.50	44.55	47.17	49.48	51.64	53.68	55.61	57.45	59.21

Compound	Formula	State	1,100	1,200	1,250	1,300	1,400	1,500	1,750	2,000	2,500	3,000	3,500	4,000	4,500	5,000
			Entropy, $S°$, in calories per degree mole													
Oxygen	O_2	Gas	58.992	59.730	60.079	60.419	61.061	61.659	63.015	64.212	66.250	67.968	69.458	70.762	71.920	72.991
Hydrogen	H_2	do	40.395	41.035	41.344	41.632	42.190	42.720	43.928	45.005	46.868	48.448	49.818	51.030	52.115	53.099
Water	H_2O	do	56.551	57.449	57.880	58.299	59.105	59.873	61.65	63.26	66.07	68.45	--------	--------	--------	--------
Nitrogen	N_2	do	55.259	55.955	56.287	56.606	57.215	57.786	59.082	60.228	62.163	63.770	65.141	66.338	67.402	68.351
Carbon (graphite)	C	Solid	6.342	6.807	7.031	7.247	7.663	8.057	--------	--------	--------	--------	--------	--------	--------	--------
Carbon (diamond)	C	do	5.18	5.63	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
Carbon monoxide	CO	Gas	56.878	57.586	57.919	58.243	58.860	59.436	60.744	61.896	63.845	65.459	66.835	68.037	69.100	70.056
Carbon dioxide	CO_2	do	65.583	66.746	67.301	67.836	68.857	69.817	72.00	73.92	77.19	80.09	82.27	--------	--------	--------
Methane	CH_4	do	60.89	62.50	63.28	64.04	65.51	66.93	--------	--------	--------	--------	--------	--------	--------	--------

TABLE 6.—*Values of the heat content,* $(H^\circ - H^\circ_0)$, *for* O_2 *(gas),* H_2 *(gas),* H_2O *(gas),* N_2 *(gas),* C *(solid, graphite),* C *(solid, diamond),* CO *(gas),* CO_2 *(gas), and* CH_4 *(gas)*

Compound	Formula	State	Temperature in degrees Kelvin													
			0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Heat content, $(H^\circ - H^\circ_0)$, in calories per mole													
Oxygen	O_2	Gas	0	--------	--------	1384.42	1732.7	2069.78	2082.72	2792.4	3524.2	4279.2	5057.4	5854.1	6669.6	7497.0
Hydrogen	H_2	do	0	--------	--------	--------	1694.28	2023.81	2036.47	2731.0	3429.5	4128.6	4831.5	5537.4	6248.0	6965.8
Water	H_2O	do	0	--------	--------	--------	--------	2365.1	2379.9	3190.0	4019.5	4873.2	5755.4	6666.4	7606.8	8580.0
Nitrogen	N_2	do	0	--------	--------	1389.30	1737.1	2072.27	2085.09	2782.4	3485.0	4198.0	4925.3	5668.6	6428.0	7202.5
Carbon (graphite)	C	Solid	0	14.451	43.155	91.973	162.468	251.56	255.31	502.6	820.8	1198.1	1622.0	2081.7	2569.4	3074.6
Carbon (diamond)	C	do	0	1.664	8.880	29.058	68.873	128.13	130.81	325	602	950	1355	1804	2284	2782
Carbon monoxide	CO	Gas	0	--------	--------	1389.40	1737.38	2072.63	2085.45	2783.8	3490.0	4209.5	4945.8	5699.8	6470.6	7256.5
Carbon dioxide	CO_2	do	0	--------	--------	--------	--------	2238.11	2254.6	3194.8	4222.8	5322.4	6481.3	7689.4	8939.9	10222
Methane	CH_4	do	0	--------	--------	--------	--------	2397	2413	3323	4365	5549	6871	8321	9887	11560

Compound	Formula	State	1,100	1,200	1,250	1,300	1,400	1,500	1,750	2,000	2,500	3,000	3,500	4,000	4,500	5,000
			Heat content, $(H^\circ - H^\circ_0)$, in calories per mole													
Oxygen	O_2	Gas	8335.2	9183.9	9611.6	10041.0	10905.1	11776.4	13980	16219	20799	25500	30308	35215	40183	45220
Hydrogen	H_2	do	7692.0	8427.5	8798.4	9173.2	9928.7	10694.2	12653.7	14672	18851	23186	27637	32168	36780	41449
Water	H_2O	do	9579.9	10613	11140	11675	12762	13876	16748	19760	26050	32580	--------	--------	--------	--------
Nitrogen	N_2	do	7991.5	8792.8	9197.5	9604.7	10425.4	11253.6	13357	15499	19839	24245	28695	33178	37690	42202
Carbon (graphite)	C	Solid	3596	4130	4403	4680	5242	5814	--------	--------	--------	--------	--------	--------	--------	--------
Carbon (diamond)	C	do	3289	3802	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
Carbon monoxide	CO	Gas	8056.2	8867.8	9277.6	9689.9	10520.9	11358.8	13481	15636	20007	24434	28900	33395	37907	42452
Carbon dioxide	CO_2	do	11536	12872	13551	14234	15611	17004	20542	24144	31480	38950	46520	--------	--------	--------
Methane	CH_4	do	13320	15170	16130	17100	19090	21130	--------	--------	--------	--------	--------	--------	--------	--------

TABLE 7.—*Values of the heat capacity, $C_p°$ for O_2 (gas), H_2 (gas), H_2O (gas), N_2 (gas), C (solid, graphite), C (solid, diamond), CO (gas), CO_2 (gas), and CH_4 (gas)*

Compound	Formula	State	Temperature in degrees Kelvin 0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Heat capacity, $C_p°$, in calories per degree mole													
Oxygen	O_2	Gas	0	--------	--------	6.961	6.970	7.017	7.019	7.194	7.429	7.670	7.885	8.064	8.212	8.335
Hydrogen	H_2	do	0	--------	--------	--------	6.769	6.892	6.895	6.974	6.993	7.008	7.035	7.078	7.139	7.217
Water	H_2O	do	0	--------	--------	--------	--------	8.025	8.026	8.185	8.415	8.677	8.959	9.254	9.559	9.869
Nitrogen	N_2	do	0	--------	--------	6.957	6.959	6.960	6.961	6.991	7.070	7.197	7.351	7.512	7.671	7.816
Carbon (graphite)	C	Solid	0	0.394	0.767	1.190	1.632	2.066	2.083	2.851	3.496	4.03	4.43	4.75	4.98	5.14
Carbon (diamond)	C	do	0	0.0673	0.246	0.587	1.013	1.449	1.466	2.38	3.14	3.79	4.29	4.66	4.90	5.03
Carbon monoxide	CO	Gas	0	--------	--------	6.956	6.958	6.965	6.965	7.013	7.120	7.276	7.451	7.624	7.787	7.932
Carbon dioxide	CO_2	do	0	--------	--------	--------	--------	8.874	8.894	9.871	10.662	11.311	11.849	12.300	12.678	12.995
Methane	CH_4	do	0	--------	--------	--------	--------	8.536	8.552	9.736	11.133	12.546	13.88	15.10	16.21	17.21

Compound	Formula	State	1,100	1,200	1,250	1,300	1,400	1,500	1,750	2,000	2,500	3,000	3,500	4,000	4,500	5,000
			Heat capacity, $C_p°$, in calories per degree mole													
Oxygen	O_2	Gas	8.440	8.530	8.570	8.608	8.676	8.739	8.885	9.024	9.305	9.518	9.711	9.879	10.003	10.105
Hydrogen	H_2	do	7.308	7.404	7.454	7.505	7.610	7.713	7.957	8.175	8.526	8.791	8.993	9.151	9.282	9.389
Water	H_2O	do	10.172	10.467	10.611	10.749	11.015	11.263	11.80	12.24	12.9	13.3	--------	--------	--------	--------
Nitrogen	N_2	do	7.947	8.063	8.116	8.165	8.253	8.330	8.486	8.602	8.759	8.862	8.934	8.989	9.036	9.076
Carbon (graphite)	C	Solid	5.27	5.42	5.50	5.57	5.67	5.76	--------	--------	--------	--------	--------	--------	--------	--------
Carbon (diamond)	C	do	5.10	5.16	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
Carbon monoxide	CO	Gas	8.058	8.167	8.218	8.265	8.349	8.419	8.561	8.665	8.806	8.899	8.963	9.015	9.059	9.099
Carbon dioxide	CO_2	do	13.26	13.49	13.59	13.68	13.85	13.99	14.3	14.5	14.8	15.0	15.2	--------	--------	--------
Methane	CH_4	do	18.09	18.88	19.23	19.57	20.18	20.71	--------	--------	--------	--------	--------	--------	--------	--------

IV. HEAT OF FORMATION, FREE ENERGY OF FORMATION, AND THE EQUILIBRIUM CONSTANT OF FORMATION

1. METHOD OF CALCULATION

Values of ΔH_0°, the increment in heat content for the given reaction, with all the reactants and products in their appropriate standard states at 0° K, were calculated by combining values of $\Delta H_{298.16}^\circ$, the increment in heat content for the given reaction at 25° C, with values of $H_{298.16}^\circ - H_0^\circ$ for the reactants and products, by means of the relation

$$\Delta H_0^\circ = \Delta H_{298.16}^\circ - \Delta(H_{298.16}^\circ - H_0^\circ), \tag{11}$$

where the last term on the right is the sum for the products less the sum for the reactants of $H_{298.16}^\circ - H_0^\circ$, the heat content at 298.16° K (25° C) less that at 0° K.

Values of ΔH° for the given reaction at other temperatures were then calculated by means of the relation

$$\Delta H^\circ = \Delta H_0^\circ + \Delta(H^\circ - H_0^\circ). \tag{12}$$

Values of ΔF°, the increment in free energy for the given reaction, with all the reactants and products in their appropriate standard states at the given temperature, were calculated by combining values of ΔH_0° for the given reaction with appropriate values of $(F^\circ - H_0^\circ)/T$, the free-energy function, by means of the relation:

$$\Delta F^\circ/T = \Delta H_0^\circ/T + \Delta[(F^\circ - H_0^\circ)/T], \tag{13}$$

where the last term on the right is the sum for the products less the sum for the reactants of $(F^\circ - H_0^\circ)/T$, the free-energy function at the given temperature.

Values of the equilibrium constant, and its logarithm, for the given reaction, were calculated from the relation [40]

$$\Delta F^\circ = -RT \ln K. \tag{14}$$

2. DATA USED IN THE CALCULATIONS

The following data were used in calculating the heat and free energy of formation of H_2O(liq) at 25° C and of the formation of H_2O (gas), CO (gas), CO_2 (gas), and CH_4 (gas) at various temperatures to 1,500° K:

For the heat of formation of liquid water,

$$H_2(\text{gas}) + 1/2\ O_2(\text{gas}) = H_2O(\text{liq}), \tag{15}$$

the value previously reported from this laboratory [41] was corrected to the present molecular weight of water, yielding for the formation of liquid water according to eq 15:

$$\Delta H^\circ_{298\cdot16} = -68{,}317.4 \pm 9.6 \text{ cal/mole.} \tag{16}$$

On the basis of the present molecular weight, the values previously reported for the standard heat, free energy, and entropy of vaporization of water at 25° C [41], including a small change resulting from an improved value for the vapor pressure of water at 25° C [42], become

$$H_2O(\text{liq}) = H_2O(\text{gas}). \tag{17}$$

$$\Delta H^\circ_{298\cdot16} = 10{,}519.5 \pm 3.1 \text{ cal/mole.} \tag{18}$$

$$\Delta F^\circ_{298\cdot16} = 2{,}054.8 \pm 1.0 \text{ cal/mole.} \tag{19}$$

$$\Delta S^\circ_{298\cdot16} = 28.390 \pm 0.012 \text{ cal/deg mole.} \tag{20}$$

A new value for the heat of formation of carbon dioxide was recently reported [43]:

$$C(\text{solid, graphite}) + O_2(\text{gas}) = CO_2(\text{gas}). \tag{21}$$

$$\Delta H^\circ_{298\cdot16} = -94{,}051.8 \pm 10.8 \text{ cal/mole.} \tag{22}$$

The value previously reported [41] for the heat of combustion of carbon monoxide to carbon dioxide remains unchanged:

$$CO(\text{gas}) + 1/2\ O_2(\text{gas}) = CO_2(\text{gas}). \tag{23}$$

$$\Delta H^\circ_{298\cdot16} = -67{,}636.1 \pm 28.7 \text{ cal/mole.} \tag{24}$$

Combination of eq 21, 22, 23, and 24 yields a new value for the heat of formation of carbon monoxide:

$$C(\text{solid, graphite}) + 1/2\ O_2(\text{gas}) = CO(\text{gas}). \tag{25}$$

$$\Delta H^\circ_{298\cdot16} = -26{,}415.7 \pm 30.7 \text{ cal/mole.} \tag{26}$$

The value for the heat of formation of methane is taken from reference [44]:

$$C(\text{solid, graphite}) + 2H_2(\text{gas}) = CH_4(\text{gas}). \tag{27}$$

$$\Delta H^\circ_{298\cdot16} = -17{,}889 \pm 75 \text{ cal/mole.} \tag{28}$$

3. RESULTS FOR H_2O, CO, CO_2, AND CH_4

The resulting values of the thermodynamic properties for the formation of H_2O(gas), CO(gas), CO_2(gas), and CH_4(gas), from the elements, O_2(gas), H_2(gas), and C(solid, graphite), are presented in table 8, which gives values of the heat of formation, ΔHf°, the free energy of formation, ΔFf°, the equilibrium constant of formation, Kf, and the logarithm of the equilibrium constant of formation, $\log_{10}Kf$, all to 1,500° K.

For the formation of liquid water from its elements at 25° C, the values of the standard heat, free energy, and entropy of formation are

$$H_2\ (\text{gas}) + 1/2\ O_2\ (\text{gas}) = H_2O\ (\text{liq}). \tag{29}$$

$$\Delta H_{298.16} = -68{,}317.4\ \pm 9.6\ \text{cal/mole}. \tag{30}$$

$$\Delta F^{\circ}_{6298.1} = -56{,}689.9\ \pm 11.2\ \text{cal/mole}. \tag{31}$$

$$\Delta S^{\circ}_{298.16} = -38.997\ \pm 0.019\ \text{cal/mole}. \tag{32}$$

V. HEAT AND FREE ENERGY OF TRANSITION OF GRAPHITE INTO DIAMOND

The value for the heat of transition of graphite into diamond at 25° C is taken from reference [43]:

$$C\ (\text{solid, graphite}) = C\ (\text{solid, diamond}) \tag{33}$$

$$\Delta H^{\circ}_{298.16} = 453.2\ \pm 20.3\ \text{cal/mole}. \tag{34}$$

From the foregoing value and the values for diamond and graphite given in tables 3, 4, 5, and 6, values were calculated for the change in heat content and free energy for the transition of graphite into diamond at 1 atmosphere, as presented in table 9.

TABLE 9.—*Values of the change in heat content and free energy for the transition of graphite into diamond, at a pressure of 1 atmosphere*

C (solid, graphite) = C (solid, diamond)	Temperature in degrees Kelvin											
	0	298. 16	300	400	500	600	700	800	900	1, 000	1, 100	1, 200
Heat of reaction, ΔH°, in cal/mole	576. 6	453. 2	452. 1	399. 0	358	328	310	299	291	284	270	249
Free energy of reaction, ΔF°, in cal/mole	576. 6	685. 0	686. 7	774. 0	873	978	1, 089	1, 201	1, 314	1, 428	1, 543	1, 663

The expressions for the thermal expansion and compressibility of graphite and diamond have been reported previously [45]. Assuming that $(1/V)\ (\partial V/\partial P)_T$ for graphite and diamond are constants independent of temperature and pressure, these values may be combined with the thermodynamic relation $(\partial \Delta F/\partial P)_T = \Delta V$ to calculate the change in free energy for the transition of graphite to diamond at temperatures up to 1,200° K and pressures up to 20,000 atmospheres:

$$\Delta F^{p} = \Delta F^{\circ} + \Delta(F^{p} - F^{\circ}). \tag{35}$$

TABLE 8.—*Values of the heat of formation, $\Delta Hf°$, free energy of formation, $\Delta Ff°$, logarithm of the equilibrium constant of formation, $\log_{10}Kf$, and the equilibrium constant of formation, Kf, of H_2O (gas), CO (gas), CO_2 (gas) and CH_4 (gas), from the elements in their standard states*

Reaction	Temperature in degrees Kelvin														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Heat of formation, $\Delta Hf°$, in kilocalories per mole														
H_2(gas)+1/2O_2 (gas)=H_2O (gas)	−57.1043	−57.7979	−57.8022	−58.042	−58.276	−58.499	−58.709	−58.902	−59.080	−59.239	−59.384	−59.511	−59.623	−59.724	−59.811
C (solid, graphite)+1/2O_2 (gas)=CO (gas)	−27.2019	−26.4157	−26.4131	−26.317	−26.295	−26.330	−26.407	−26.511	−26.635	−26.768	−26.909	−27.056	−27.212	−27.376	−27.545
C (solid, graphite)+O_2 (gas)=CO_2 (gas)	−93.9686	−94.0518	−94.0520	−94.069	−94.091	−94.123	−94.167	−94.215	−94.268	−94.318	−94.364	−94.410	−94.456	−94.505	−94.555
C (solid, graphite)+2H_2 (gas)=CH_4 (gas)	−15.987	−17.889	−17.903	−18.629	−19.302	−19.893	−20.401	−20.823	−21.166	−21.43	−21.65	−21.79	−21.92	−22.00	−22.06
	Free energy of formation, $\Delta Ff°$, in kilocalories per mole														
H_2(gas)+1/2O_2 (gas)=H_2O (gas)	−57.1043	−54.6351	−54.6152	−53.516	−52.358	−51.154	−49.912	−48.643	−47.349	−46.036	−44.710	−43.370	−42.017	−40.661	−39.296
C (solid, graphite)+1/2O_2 (gas)=CO (gas)	−27.2019	−32.8079	−32.8464	−35.007	−37.184	−39.358	−41.526	−43.677	−45.816	−47.942	−50.053	−52.153	−54.235	−56.308	−58.370
C (solid, graphite)+O_2 (gas)=CO_2 (gas)	−93.9686	−94.2598	−94.2603	−94.325	−94.392	−94.444	−94.497	−94.539	−94.578	−94.610	−94.637	−94.661	−94.677	−94.690	−94.707
C (solid, graphite)+2H_2 (gas)=CH_4 (gas)	−15.987	−12.140	−12.104	−10.048	−7.840	−5.49	−3.05	−0.55	+2.01	4.61	7.22	9.85	12.50	15.14	17.80
	Logarithm of the equilibrium constant of formation, $\log_{10}Kf$														
H_2(gas)+1/2O_2 (gas)=H_2O (gas)		40.04695	39.78683	29.23972	22.88551	18.63228	15.58315	13.22846	11.49776	10.06104	8.88300	7.89864	7.06367	6.34747	5.72542
C (solid, graphite)+1/2O_2 (gas)=CO (gas)		24.04790	23.92845	19.12672	16.25283	14.33621	12.96479	11.93193	11.12559	10.47772	9.94448	9.49826	9.11762	8.78999	8.50449
C (solid, graphite)+O_2 (gas)=CO_2 (gas)		69.09145	68.66801	51.53648	41.25820	34.40107	29.50309	25.82664	22.96647	20.67675	18.80256	17.23998	15.91654	14.78159	13.79863
C (solid, graphite)+2H_2 (gas)=CH_4 (gas)		8.8985	8.8177	5.4899	3.4268	2.0001	0.9526	0.1494	−0.4881	−1.0075	−1.4345	−1.7936	−2.1006	−2.3638	−2.5927
	Equilibrium constant of formation, Kf														
H_2(gas)+1/2O_2 (gas)=H_2O (gas)		1.114×10^{40}	6.121×10^{39}	1.737×10^{29}	7.683×10^{22}	4.288×10^{18}	3.830×10^{15}	1.943×10^{13}	3.146×10^{11}	1.151×10^{10}	7.638×10^{8}	7.918×10^{7}	1.158×10^{7}	2.226×10^{6}	5.314×10^{5}
C (solid, graphite)+1/2O_2 (gas)=CO (gas)		1.117×10^{24}	8.481×10^{23}	1.339×10^{19}	1.790×10^{16}	2.169×10^{14}	9.221×10^{12}	8.549×10^{11}	1.335×10^{11}	3.004×10^{10}	8.800×10^{9}	3.150×10^{9}	1.311×10^{9}	6.166×10^{8}	3.195×10^{8}
C (solid, graphite)+O_2 (gas) =CO_2 (gas)		1.234×10^{69}	4.656×10^{68}	3.439×10^{51}	1.812×10^{41}	2.518×10^{34}	3.185×10^{29}	6.709×10^{25}	9.257×10^{22}	4.751×10^{20}	6.347×10^{18}	1.738×10^{17}	8.252×10^{15}	6.040×10^{14}	6.290×10^{13}
C (solid, graphite)+2H_2 (gas) =CH_4 (gas)		7.916×10^{8}	6.572×10^{8}	3.090×10^{5}	2.672×10^{3}	100	8.966	1.411	0.3250	9.829×10^{-2}	3.677×10^{-2}	1.608×10^{-2}	7.932×10^{-3}	4.327×10^{-3}	2.554×10^{-3}

TABLE 11.—*Values of the logarithm of the equilibrium constant, $\log_{10}K$, and the equilibrium constant, K, for some reactions involving O_2, H_2, H_2O, C(graphite), CO, CO_2, and CH_4*

Reaction	Temperature in degrees Kelvin														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Logarithm of the equilibrium constant, $\log_{10}K$														
C (solid, graphite)+CO_2(gas)=2CO (gas)		−20.99575	−20.81089	−13.28281	−8.75242	−5.72851	−3.57358	−1.96284	−0.71538	+0.27865	1.08638	1.75658	2.31863	2.79835	3.21033
C (solid, graphite)+H_2O (gas)=CO (gas)+H_2 (gas)		−15.99896	−15.85786	−10.11277	−6.65217	−4.29593	−2.61852	−1.35664	−.37226	+.41655	1.06373	1.59959	2.05385	2.44243	2.77906
CO (gas)+1/2O_2 (gas)=CO_2 (gas)		+45.04367	44.73973	32.40960	25.00541	20.06491	16.53817	13.89475	11.84070	10.19920	8.85796	7.74189	6.79887	5.99165	5.29440
CO (gas)+H_2O (gas)=CO_2 (gas)+H_2 (gas)		+4.99679	4.95303	3.17004	2.10025	1.43258	0.95506	0.60620	0.34312	0.13790	−0.02484	−0.15699	−0.26478	−0.35592	−0.43127
CH_4 (gas)+1/2O_2 (gas)=CO (gas)+2H_2 (gas)		+15.14943	15.11042	13.62866	12.82615	12.33631	12.01203	11.78248	11.61365	11.48514	11.37881	11.29165	11.21808	11.15376	11.09715
CH_4 (gas)+CO_2 (gas)=2CO (gas)+2H_2 (gas)		−29.89351	−29.62931	−18.78203	−12.17882	−7.72859	−4.52613	−2.11227	−0.22705	+1.28594	2.52066	3.54995	4.41921	5.16211	5.80289
CH_4 (gas)+H_2O (gas)=CO (gas)+3H_2 (gas)		−24.89745	−24.67628	−15.61144	−10.05889	−6.29601	−3.57077	−1.50580	+.11607	1.42428	2.49602	3.39314	4.15460	4.80634	5.37177
CH_4 (gas)+2H_2O (gas)=CO_2 (gas)+4H_2 (gas)		−19.90067	−19.72325	−12.44091	−7.93898	−4.86343	−2.61571	−0.89960	+.45919	1.56218	2.47118	3.23615	3.88982	4.45042	4.94050
	Equilibrium constant, K														
C (solid, graphite)+CO_2 (gas)=2CO (gas)		1.012×10^{-21}	1.546×10^{-21}	5.214×10^{-14}	1.768×10^{-9}	1.868×10^{-6}	2.669×10^{-4}	1.098×10^{-2}	0.1926	1.900	12.20	57.09	2.083×10^{2}	6.286×10^{2}	1.623×10^{3}
C (solid, graphite)+H_2O (gas)=CO (gas)+H_2 (gas)		1.002×10^{-16}	1.387×10^{-16}	7.713×10^{-11}	2.228×10^{-7}	5.059×10^{-5}	2.407×10^{-3}	4.399×10^{-2}	.4244	2.609	11.58	39.77	1.135×10^{2}	2.770×10^{2}	6.013×10^{2}
CO (gas)+1/2O_2 (gas)=CO_2 (gas)		1.106×10^{45}	5.492×10^{44}	2.568×10^{32}	1.013×10^{25}	1.161×10^{20}	3.453×10^{16}	7.848×10^{13}	6.930×10^{11}	1.582×10^{10}	7.210×10^{8}	5.519×10^{7}	6.293×10^{6}	9.810×10^{5}	1.970×10^{5}
CO (gas)+H_2O (gas)=CO_2 (gas)+H_2 (gas)		9.926×10^{4}	8.975×10^{4}	1.479×10^{3}	1.260×10^{2}	27.08	9.017	4.038	2.204	1.374	0.9444	0.6966	0.5435	0.4406	0.3704
CH_4 (gas)+1/2O_2 (gas)=CO (gas)+2H_2 (gas)		1.411×10^{15}	1.290×10^{15}	4.253×10^{13}	6.710×10^{12}	2.169×10^{12}	1.028×10^{12}	6.060×10^{11}	4.108×10^{11}	3.056×10^{11}	2.392×10^{11}	1.957×10^{11}	1.652×10^{11}	1.425×10^{11}	1.251×10^{11}
CH_4 (gas)+CO_2 (gas)=2CO (gas)+2H_2 (gas)		1.278×10^{-30}	2.348×10^{-30}	1.652×10^{-19}	6.625×10^{-13}	1.868×10^{-8}	2.978×10^{-5}	7.722×10^{-3}	0.5929	19.32	3.316×10^{2}	3.548×10^{3}	2.626×10^{4}	1.452×10^{5}	6.352×10^{5}
CH_4 (gas)+H_2O (gas)=CO (gas)+3H_2 (gas)		1.266×10^{-25}	2.107×10^{-25}	2.447×10^{-16}	8.732×10^{-11}	5.058×10^{-7}	2.687×10^{-4}	3.120×10^{-2}	1.306	26.56	3.133×10^{2}	2.473×10^{3}	1.428×10^{4}	6.402×10^{4}	2.354×10^{5}
CH_4 (gas)+2H_2O (gas)=CO_2 (gas)+4H_2 (gas)		1.257×10^{-20}	1.891×10^{-20}	3.623×10^{-13}	1.151×10^{-8}	1.369×10^{-5}	2.423×10^{-3}	0.1260	2.879	36.49	2.959×10^{2}	1.723×10^{3}	7.759×10^{3}	2.821×10^{4}	8.720×10^{4}

The first term on the right is given in table 9, and the second term on the right is the increment in free energy from 1 atmosphere to P atmospheres for diamond less that of graphite, at a given temperature. Values of $(F^p - F^\circ)$ and $\Delta(F^p - F^\circ)$ for various pressures and temperatures are given by the relations:

For C (solid, graphite)—

$$(F^p - F^\circ) = [0.12843 + 7.617 \times 10^{-7} T + 4.848 \times 10^{-10} T^2] \\ [(P-1) - 1.52 \times 10^{-6}(P^2 - 1) + 1.54 \times 10^{-12}(P^3 - 1)] \text{ cal/mole,} \quad (36)$$

For C (solid, diamond)—

$$(F^p - F^\circ) = [0.082777 - 1.505 \times 10^{-7} T + 5.631 \times 10^{-10} T^2 \\ + 3.6224 \times 10^{-13} T^3][(P-1) - 8.0 \times 10^{-8}(P^2 - 1) \\ + 4.0 \times 10^{-15}(P^3 - 1)] \text{ cal/mole,} \quad (37)$$

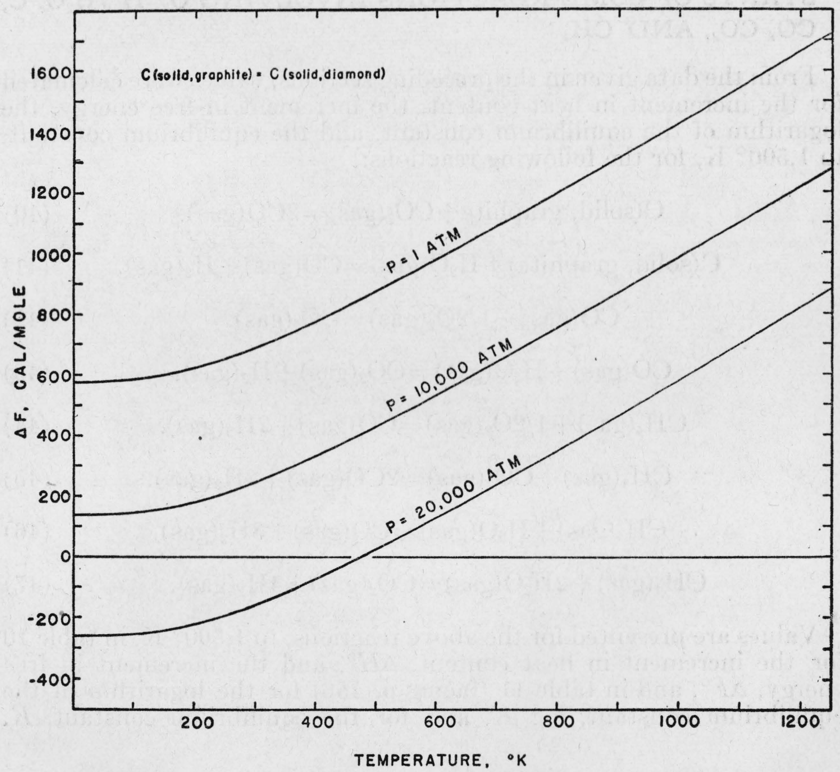

FIGURE 1.—*Plot of the free energy change for the transition of graphite into diamond.*

The scale of ordinates gives the increment in free energy, ΔF°, in cal/mole, for the transition, C (solid, graphite) = C (solid, diamond). The scale of abscissas gives the absolute temperature in degrees Kelvin. As indicated, the three curves are for pressures of 1, 10,000, and 20,000 atmospheres. Values below zero indicate, within the limits of uncertainty, the region in which diamond is thermodynamically more stable than graphite. See text.

For the transition—

$$\text{C (solid, graphite)} = \text{C (solid, diamond)} \qquad (38)$$

$$\begin{aligned}\Delta(F^p - F^\circ) = &-[0.045653 + 9.122\times10^{-7}T - 7.83\times10^{-11}T^2 \\ &-3.6224\times10^{-13}T^3][P-1] + [1.886\times10^{-6} + 1.17\times10^{-12}T \\ &+6.92\times10^{-16}T^2 - 2.9\times10^{-20}T^3][P^2-1] - [1.974\times10^{-13} \\ &+1.174\times10^{-18}T + 7.44\times10^{-22}T^2 - 1.45\times10^{-27}T^3][P^3-1]\text{cal/mole.}\end{aligned} \qquad (39)$$

In eq 36, 37, and 39, P is in atmospheres, and T is in degrees Kelvin.

Values of the change in free energy for the transition of graphite into diamond at various temperatures and pressures are plotted in figure 1.

VI. HEATS, FREE ENERGIES, AND EQUILIBRIUM CONSTANTS OF SOME REACTIONS INVOLVING O_2, H_2, H_2O, C, CO, CO_2, AND CH_4

From the data given in the preceding sections, values were calculated for the increment in heat content, the increment in free energy, the logarithm of the equilibrium constant, and the equilibrium constant, to 1,500° K, for the following reactions:

$$\text{C(solid, graphite} + CO_2\text{(gas)} = 2CO\text{(gas)}. \qquad (40)$$

$$\text{C(solid, graphite)} + H_2O\text{(gas)} = CO\text{(gas)} + H_2\text{(gas)}. \qquad (41)$$

$$CO\text{(gas)} + 1/2O_2\text{(gas)} = CO_2\text{(gas)}. \qquad (42)$$

$$CO\text{(gas)} + H_2O\text{(gas)} = CO_2\text{(gas)} + H_2\text{(gas)}. \qquad (43)$$

$$CH_4\text{(gas)} + 1/2O_2\text{(gas)} = CO\text{(gas)} + 2H_2\text{(gas)}. \qquad (44)$$

$$CH_4\text{(gas)} + CO_2\text{(gas)} = 2CO\text{(gas)} + 2H_2\text{(gas)}. \qquad (45)$$

$$CH_4\text{(gas)} + H_2O\text{(gas)} = CO\text{(gas)} + 3H_2\text{(gas)}. \qquad (46)$$

$$CH_4\text{(gas)} + 2H_2O\text{(gas)} = CO_2\text{(gas)} + 4H_2\text{(gas)}. \qquad (47)$$

Values are presented for the above reactions, to 1,500° K, in table 10 for the increment in heat content, ΔH°, and the increment in free energy, ΔF°, and in table 11 (facing p. 156) for the logarithm of the equilibrium constant, $\log_{10}K$, and for the equilibrium constant, K.

TABLE 10.—*Values of the heat, $\Delta H°$, and free energy, $\Delta F°$, for some reactions involving* O_2, H_2, H_2O, C *(graphite)*, CO, CO_2, *and* CH_4

Reaction	Temperature in degrees Kelvin														
	0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
	Heat of reaction, $\Delta H°$, in calories per mole														
C (solid, graphite)+CO_2 (gas)=2CO (gas)	39565	41220	41226	41435	41501	41463	41353	41193	40997	40781	40545	40298	40031	39754	39464
C (solid, graphite)+H_2O (gas)=CO (gas)+H_2 (gas)	29902	31382	31389	31725	31981	32169	32302	32391	32445	32470	32474	32454	32411	32348	32265
CO (gas)+1/2O_2 (gas)=CO_2 (gas)	−66767	−67636	−67639	−67752	−67796	−67793	−67760	−67704	−67632	−67550	−67455	−67355	−67243	−67129	−67010
CO (gas)+H_2O (gas)=CO_2 (gas)+H_2 (gas)	−9662	−9838	−9837	−9710	−9520	−9294	−9051	−8802	−8552	−8311	−8071	−7844	−7620	−7406	−7199
CH_4 (gas)+1/2O_2 (gas)=CO (gas)+2H_2 (gas)	−11215	−8527	−8511	−7688	−6993	−6437	−6006	−5689	−5470	−5335	−5262	−5254	−5299	−5379	−5486
CH_4 (gas)+CO_2 (gas)=2 CO (gas)+2H_2 (gas)	55552	59109	59128	60063	60803	61356	61754	62016	62162	62214	62192	62100	61944	61750	61524
CH_4 (gas)+H_2O (gas)=CO (gas)+3H_2 (gas)	45889	49271	49291	50353	51283	52062	52703	53214	53610	53903	54122	54257	54324	54344	54325
CH_4 (gas)+2H_2O (gas)=CO_2 (gas)+4H_2 (gas)	36227	39433	39454	40643	41763	42768	43652	44412	45058	45592	46051	46413	46704	46938	47126
	Free energy of reaction, $\Delta F°$, in calories per mole														
C (solid, graphite)+CO_2 (gas)=2CO (gas)	39565	28644	28567	24311	20024	15727	11446	7185	2946	−1275	−5468	−9645	−13792	−17926	−22034
C (solid, graphite)+H_2O (gas)=CO (gas)+H_2 (gas)	29902	21827	21768	18509	15219	11794	8387	4966	1533	−1906	−5354	−8783	−12217	−15646	−19074
CO (gas)+1/2O_2 (gas)=CO_2 (gas)	−66767	−61452	−61414	−59318	−57208	−55086	−52971	−50862	−48761	−46668	−44584	−42509	−40442	−38382	−36338
CO (gas)+H_2O (gas)=CO_2 (gas)+H_2 (gas)	−9662	−6817	−6799	−5802	−4850	−3933	−3059	−2219	−1413	−631	+125	862	1575	2280	2960
CH_4 (gas)+1/2O_2 (gas)=CO (gas)+2H_2 (gas)	−11215	−20668	−20742	−24944	−29344	−33868	−38474	−43130	−47826	−52552	−57272	−62000	−66729	−71450	−76165
CH_4 (gas)+CO_2 (gas)=2CO (gas)+2H_2 (gas)	55552	40783	40672	34376	27863	21218	14497	7732	935	−5884	−12687	−19492	−26287	−33068	−39828
CH_4 (gas)+H_2O (gas)=CO (gas)+3H_2 (gas)	45889	33967	33873	28573	23013	17285	11437	5512	−478	−6517	−12563	−18631	−24713	−30789	−36869
CH_4 (gas)+2H_2O (gas)=CO_2 (gas)+4H_2 (gas)	36227	27150	27074	22771	18163	13352	8378	3293	−1891	−7148	−12438	−17769	−23138	−28509	−33909

In figure 2 are plotted the values of the logarithm of the equilibrium constant for these reactions and for reaction (27).

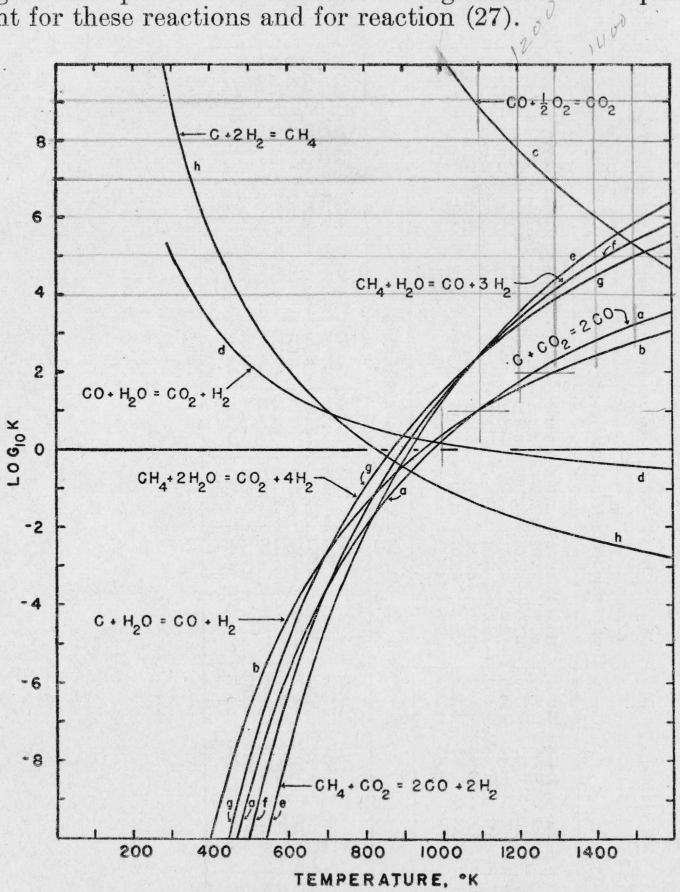

FIGURE 2.—*Plot of the logarithm of the equilibrium constant for eight reaction involving* O_2, H_2, H_2O, C *(graphite)*, CO, CO_2, *and* CH_4.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant, $\log_{10}K$, for the given reaction. The scale of abscissas gives the temperature in degrees Kelvin. The curves apply to the following reactions (see text):

(a) C(solid, graphite)+CO_2(gas)=2CO(gas).
(b) C(solid, graphite)+H_2O(gas)=CO(gas)+H_2(gas).
(c) CO(gas)+1/2O_2(gas)=CO_2(gas).
(d) CO(gas)+H_2O(gas)=CO_2(gas)+H_2(gas).
(e) CH_4(gas)+CO_2(gas)=2CO(gas)+2H_2(gas).
(f) CH_4(gas)+H_2O(gas)=CO(gas)+3H_2(gas).
(g) CH_4(gas)+2H_2O(gas)=CO_2(gas)+4H_2(gas).
(h) C(solid, graphite)+2H_2(gas)=CH_4(gas).

VII. REFERENCES

[1] E. F. Mueller and F. D. Rossini, Am. J. Phys. **12,** 1 (1944).
[2] G. K. Burgess, BS J. Research **1,** 635 (1928) RP22.
[3] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, J. Am. Chem. Soc. **63,** 845 (1941).
[4] C. S. Cragoe, J. Research NBS **26,** 495 (1941) RP1393.
[5] E. C. Crittenden, National Bureau of Standards (1943), Private communication; H. L. Curtis, J. Research NBS **33,** 235 (1944) RP1606.
[6] R. T. Birge, Rev. Modern Phys. **13,** 233 (1941).
[7] R. T. Birge, Rev. Modern Phys. **1,** 1(1929).
[8] R. C. Tolman, The Principles of Statistical Mechanics (Oxford University Press, New York, N. Y., 1938.)
[9] J. E. Mayer and M. G. Mayer, Statistical Mechanics (John Wiley & Sons, Inc., New York, N. Y., 1940.)
[10] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **55,** 172 (1933).
[11] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **57,** 682 (1935).
[12] C. O. Davis and H. L. Johnston, J. Am. Chem. Soc. **56,** 1045 (1934).
[13] H. L. Johnston and C. O. Davis, J. Am. Chem. Soc. **56,** 271 (1934).
[14] W. F. Giauque, J. Am. Chem. Soc. **52,** 4816 (1930).
[15] W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. **55,** 4875 (1933).
[16] J. O. Clayton and W. F. Giauque, J. Am. Chem. Soc. **55,** 5071 (1933).
[17] A. R. Gordon, J. Chem. Phys. **2,** 65 (1934).
[18] A. R. Gordon, J. Chem. Phys. **2,** 549 (1934).
[19] L. S. Kassel, J. Am. Chem. Soc. **56,** 1838 (1934).
[20] E. B. Wilson, Jr., J. Chem. Phys. **4,** 526 (1936).
[21] K. S. Pitzer, Ind. Eng. Chem. **36,** 829 (1944).
[22] A. R. Gordon and C. Barnes, J. Chem. Phys. **1,** 297 (1933).
[23] A. R. Gordon and C. Barnes, J. Phys. Chem. **36,** 1143 (1932).
[24] W. F. Libby, J. Chem. Phys. **11,** 101 (1943).
[25] L. S. Kassel, J. Chem. Phys. **1,** 576 (1933).
[26] A. R. Gordon, J. Chem. Phys. **1,** 308 (1933).
[27] W. Nernst, Ann. Physik [4] **36,** 395 (1911).
[28] A. G. Worthing, Phys. Rev. **12,** 199 (1918).
[29] A. Magnus, Ann. Physik [4] **70,** 303 (1923).
[30] P. Schläpfer and P. Debrunner, Helv. Chim. Acta **7,** 31 (1924).
[31] C. J. Jacobs and G. S. Parks, J. Am. Chem. Soc. **56,** 1513 (1934).
[32] A. Magnus, Ann. Physik [4] **48,** 983 (1915).
[33] H. F. Weber, Ann. Physik [2] **154,** 367 (1875).
[34] H. F. Weber, Ann. Physik [2] **154,** 553 (1875).
[35] A. Magnus and A. Hodler, Ann. Physik [4] **80,** 808 (1926).
[36] K. S. Pitzer, J. Chem. Phys. **6,** 68 (1938).
[37] A. Bettendorff and A. Wüllner, Ann. Physik [2] **133,** 293 (1868).
[38] W. Nernst and F. A. Lindemann, Z. Elektrochem. **17,** 817 (1911).
[39] R. Robertson, J. J. Fox, and A. E. Martin, Proc. Roy. Soc (London) **A157,** 579 (1936).
[40] G. N. Lewis and M. Randall, Thermodynamics, p. 294 (McGraw-Hill Book Co. Inc., 1923).
[41] F. D. Rossini, J. Research NBS **22,** 407 (1939) RP1192.
[42] C. H. Meyers and C. S. Cragoe, National Bureau of Standards. Unpublished.
[43] E. J. Prosen, R. S. Jessup, and F. D. Rossini, J. Research NBS **33,** 447 (1944) RP1620.
[44] E. J. Prosen and F. D. Rossini, J. Research NBS **34,** 263 (1945) RP1642.
[45] F. D. Rossini and R. S. Jessup, J. Research NBS **21,** 491 (1938) RP1141.

WASHINGTON, October 31, 1944.