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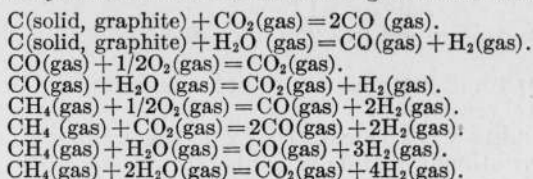
# HEATS, FREE ENERGIES, AND EQUILIBRIUM CONSTANTS OF SOME REACTIONS INVOLVING O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, C, CO, CO<sub>2</sub>, AND CH<sub>4</sub><sup>1</sup>

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### 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,  $S^\circ$ , the heat content,  $H^\circ - H_0^\circ$ , and the heat capacity,  $C_p^\circ$ , for O<sub>2</sub> (gas) to 5,000 °K, H<sub>2</sub> (gas) to 5,000 °K, H<sub>2</sub>O (gas) to 3,000 °K, N<sub>2</sub> (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<sub>2</sub> (gas) to 3,500 °K, and CH<sub>4</sub> (gas) to 1,500 °K; the standard entropy,  $S^\circ$ , for H<sub>2</sub>O (liq) at 25 °C; the heat of formation,  $\Delta H_f^\circ$ , the free energy of formation,  $\Delta F_f^\circ$ , and the equilibrium constant of formation,  $K_f$ , from the elements, for H<sub>2</sub>O (liq) at 25 °C, and for H<sub>2</sub>O (gas), CO (gas), CO<sub>2</sub> (gas), and CH<sub>4</sub> (gas), to 1,500 °K; the increment in heat content,  $\Delta H^\circ$ , and the increment in free energy,  $\Delta F^\circ$ , 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,  $\Delta H^\circ$ , the increment in free energy,  $\Delta F^\circ$ , 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:



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

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<sup>1</sup> 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."

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## 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]:<sup>4</sup>

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

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

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

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,  $(PV)_{0^\circ\text{C}}^{\text{P}=\text{0}}$ , which is equal to the product of the gas constant per mole and the absolute temperature of the ice point,  $(RT)_{0^\circ\text{C}}$ , is taken from the value calculated by Cragoe [4]:

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

The uncertainty in the foregoing relation is estimated to be  $\pm 0.002$  percent.

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

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

The uncertainty in the foregoing relation is estimated to be  $\pm 0.005$  percent.

<sup>4</sup> 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 ± 0.004 cm <sup>3</sup>	[6]
b	1 atm = 1,013,250 dyne/cm <sup>2</sup>	Definition, [2]
c	1 int. joule (NBS) = 1.00017 ± 0.00005 abs. joule	[5]
d	1 cal = 4.1833 int. joule (NBS)	Definition, [1]
e	= 4.18401 ± 0.00021 abs. joule	d, c
f	= 41.2930 ± 0.0021 cm <sup>3</sup> atm	d, c, b
g	= 0.0412918 ± 0.0000021 liter atm	d, c, b, a
h	$(PV)_{0^{\circ}\text{C}}^0 = (RT)_{0^{\circ}\text{C}} = 2271.16 \pm 0.04$ abs. joule/mole	[4]
i	= 22414.6 ± 0.4 cm <sup>3</sup> atm/mole	h, b
j	= 22.4140 ± 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 ± 0.00054 int. joule/deg mole	l, c
n	= 1.98718 ± 0.00013 cal/deg mole	l, e
o	= 82.0567 ± 0.0034 cm <sup>3</sup> atm/deg mole	l, b
p	= 0.0820544 ± 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 ± 0.0036 int. joule cm/mole	u, c
w	= 2.8585 ± 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<sup>2</sup>, 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<sup>2</sup>, 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,  $\sigma$ , is the number of ways the molecule may be superimposed upon itself by rotation of the entire molecule. For linear molecules the value of  $\sigma$  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:  $(H^\circ - H_0^\circ)/T$ ,  $C^\circ$ ,  $(F^\circ - H_0^\circ)/T$ , and  $S^\circ$  in cal/deg mole;  $T$  in  $^\circ\text{K}$ ;  $M$  in g/mole;  $I$ ,  $I_1$ ,  $I_2$ , and  $I_3$  in g-cm<sup>2</sup>;  $\sigma$ , a dimensionless integer; logarithms to the base 10.]

## TRANSLATION (OF ALL MOLECULES)

$$\begin{aligned}(H^\circ - H_0^\circ)/T &= C^\circ = 4.9680 \\ (F^\circ - H_0^\circ)/T &= -6.8635 \log M + 7.2820 - 11.4391 \log T \\ S^\circ &= 6.8635 \log M - 2.3141 + 11.4391 \log T\end{aligned}$$

## ROTATION (OF RIGID MOLECULES)

I. *Diatomic or linear polyatomic molecules.*

$$(H^\circ - H_0^\circ)/T = C^\circ = 1.9872$$

(a)  $\sigma$  (symmetry number) = 1:

$$\begin{aligned}(F^\circ - H_0^\circ)/T &= -4.5757 \log (I \times 10^{39}) + 2.7676 - 4.5757 \log T \\ S^\circ &= 4.5757 \log (I \times 10^{39}) - 0.7804 + 4.5757 \log T\end{aligned}$$

(b)  $\sigma$  (symmetry number) = 2:

$$\begin{aligned}(F^\circ - H_0^\circ)/T &= -4.5757 \log (I \times 10^{39}) + 4.1450 - 4.5757 \log T \\ S^\circ &= 4.5757 \log (I \times 10^{39}) - 2.1578 + 4.5757 \log T\end{aligned}$$

II. *Nonlinear polyatomic molecules.*

$$(H^\circ - H_0^\circ)/T = C^\circ = 2.9808$$

$$\begin{aligned}(F^\circ - H_0^\circ)/T &= -2.2878 \log (I_1 I_2 I_3 \times 10^{117}) + 4.5757 \log \sigma + 3.0140 - 6.8635 \log T \\ S^\circ &= 2.2878 \log (I_1 I_2 I_3 \times 10^{117}) - 4.5757 \log \sigma - 0.0332 + 6.8635 \log T\end{aligned}$$

## 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,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ , 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

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

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

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  $\Delta M$  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:

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

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

$$S^\circ = 1.00014 \{ (S^\circ)' - 0.00421 [T d(S^\circ)' / dT - 5/2R'] - 0.014 \} + 2.98 \Delta M/M. \quad (8)$$

$$C_p^\circ = 1.00014 \{ (C_p^\circ)' - 0.00421T d(C_p^\circ)' / dT \}. \quad (9)$$

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  $1,500^\circ$  K for graphite and to  $1,200^\circ$  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<sub>2</sub> (*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 Giaque [14], who gave values for the free-energy function. See also Gordon and Barnes [23] and Libby [24].

H<sub>2</sub>O (*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<sub>2</sub> (*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 Giaque 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 Giaque [16], who gave values for the free-energy function to 5,000° K. See also Gordon and Barnes [22], and Kassel [25].

CO<sub>2</sub> (*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<sub>4</sub> (*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<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, [N<sub>2</sub>, C, CO, CO<sub>2</sub>, AND CH<sub>4</sub>

The resulting values of the thermodynamic properties for O<sub>2</sub> (gas), H<sub>2</sub> (gas), H<sub>2</sub>O (gas), N<sub>2</sub> (gas), C (solid, graphite), C (solid, diamond), CO (gas), CO<sub>2</sub> (gas), and CH<sub>4</sub> (gas) are presented in tables 3, 4, 5, 6, and 7, which give, respectively, values of the heat-content function,  $(H^\circ - H_0^\circ)/T$ , the free-energy function,  $(F^\circ - H_0^\circ)/T$ ; the entropy,  $S^\circ$ , the heat content,  $H^\circ - H_0^\circ$ , and the heat capacity,  $C_p^\circ$ .

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:

$$S_{298-16}^\circ(\text{H}_2\text{O}(\text{liq.})) = S_{298-16}^\circ(\text{H}_2\text{O}(\text{gas})) - \Delta S_{298-16}^\circ = 16.716 \pm 0.016 \text{ cal/deg mole.} \quad (10)$$







TABLE 5.—Values of the entropy,  $S^\circ$ , 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, $S^\circ$ , 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
			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, $S^\circ$ , 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 7.—Values of the heat capacity,  $C_p^\circ$  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	Form- ula	State	Temperature in degrees Kelvin													
			0	100	150	200	250	298.16	300	400	500	600	700	800	900	1,000
			Heat capacity, $C_p^\circ$ , 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	9.569	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
			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, $C_p^\circ$ , 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										

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

##### 1. METHOD OF CALCULATION

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

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

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  $298.16^\circ \text{K}$  ( $25^\circ \text{C}$ ) less that at  $0^\circ \text{K}$ .

Values of  $\Delta H^\circ$  for the given reaction at other temperatures were then calculated by means of the relation

$$\Delta H^\circ = \Delta H_0^\circ + \Delta(H^\circ - H_0^\circ). \quad (12)$$

Values of  $\Delta F^\circ$ , 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  $\Delta H_0^\circ$  for the given reaction with appropriate values of  $(F^\circ - H_0^\circ)/T$ , the free-energy function, by means of the relation:

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

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]

$$\Delta F^\circ = -RT \ln K. \quad (14)$$

##### 2. DATA USED IN THE CALCULATIONS

The following data were used in calculating the heat and free energy of formation of  $\text{H}_2\text{O}(\text{liq})$  at  $25^\circ \text{C}$  and of the formation of  $\text{H}_2\text{O}(\text{gas})$ ,  $\text{CO}(\text{gas})$ ,  $\text{CO}_2(\text{gas})$ , and  $\text{CH}_4(\text{gas})$  at various temperatures to  $1,500^\circ \text{K}$ :

For the heat of formation of liquid water,



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:

$$\Delta H_{298.16}^{\circ} = -68,317.4 \pm 9.6 \text{ cal/mole.} \quad (16)$$

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

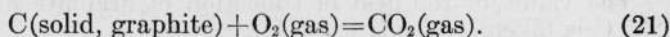


$$\Delta H_{298.16}^{\circ} = 10,519.5 \pm 3.1 \text{ cal/mole.} \quad (18)$$

$$\Delta F_{298.16}^{\circ} = 2,054.8 \pm 1.0 \text{ cal/mole.} \quad (19)$$

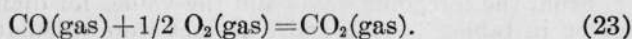
$$\Delta S_{298.16}^{\circ} = 28.390 \pm 0.012 \text{ cal/deg mole.} \quad (20)$$

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



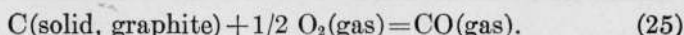
$$\Delta H_{298.16}^{\circ} = -94,051.8 \pm 10.8 \text{ cal/mole.} \quad (22)$$

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



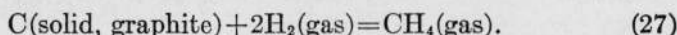
$$\Delta H_{298.16}^{\circ} = -67,636.1 \pm 28.7 \text{ cal/mole.} \quad (24)$$

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



$$\Delta H_{298.16}^{\circ} = -26,415.7 \pm 30.7 \text{ cal/mole.} \quad (26)$$

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



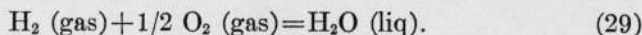
$$\Delta H_{298.16}^{\circ} = -17,889 \pm 75 \text{ cal/mole.} \quad (28)$$

### 3. RESULTS FOR H<sub>2</sub>O, CO, CO<sub>2</sub>, AND CH<sub>4</sub>

The resulting values of the thermodynamic properties for the formation of H<sub>2</sub>O(gas), CO(gas), CO<sub>2</sub>(gas), and CH<sub>4</sub>(gas), from the elements, O<sub>2</sub>(gas), H<sub>2</sub>(gas), and C(solid, graphite), are presented in

table 8, which gives values of the heat of formation,  $\Delta H_f^\circ$ , the free energy of formation,  $\Delta F_f^\circ$ , the equilibrium constant of formation,  $K_f$ , and the logarithm of the equilibrium constant of formation,  $\log_{10} K_f$ , all to  $1,500^\circ \text{K}$ .

For the formation of liquid water from its elements at  $25^\circ \text{C}$ , the values of the standard heat, free energy, and entropy of formation are



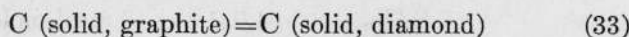
$$\Delta H_{298.16} = -68,317.4 \pm 9.6 \text{ cal/mole}. \quad (30)$$

$$\Delta F_{6298.1}^\circ = -56,689.9 \pm 11.2 \text{ cal/mole}. \quad (31)$$

$$\Delta S_{298.16}^\circ = -38.997 \pm 0.019 \text{ cal/mole}. \quad (32)$$

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

The value for the heat of transition of graphite into diamond at  $25^\circ \text{C}$  is taken from reference [43]:



$$\Delta H_{298.16}^\circ = 453.2 \pm 20.3 \text{ cal/mole}. \quad (34)$$

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, $\Delta H^\circ$ , in cal/mole.....	576.6	453.2	452.1	399.0	358	328	310	299	291	284	270	249
Free energy of reaction, $\Delta F^\circ$ , 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  $1,200^\circ \text{K}$  and pressures up to 20,000 atmospheres:

$$\Delta F^p = \Delta F^\circ + \Delta(F^p - F^\circ). \quad (35)$$

TABLE 8.—Values of the heat of formation,  $\Delta H_f^\circ$ , free energy of formation,  $\Delta F_f^\circ$ , logarithm of the equilibrium constant of formation,  $\log_{10} K_f$ , and the equilibrium constant of formation,  $K_f$ , 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, $\Delta H_f^\circ$ , 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, $\Delta F_f^\circ$ , 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, $\log_{10} K_f$															
$H_2$ (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, $K_f$															
$H_2$ (gas) + $1/2O_2$ (gas) = $H_2O$ (gas).....		$1.114 \times 10^{40}$	$6.121 \times 10^{39}$	$1.737 \times 10^{39}$	$7.683 \times 10^{32}$	$4.288 \times 10^{25}$	$3.830 \times 10^{18}$	$1.943 \times 10^{13}$	$3.146 \times 10^{11}$	$1.151 \times 10^{10}$	$7.638 \times 10^8$	$7.918 \times 10^7$	$1.158 \times 10^7$	$2.226 \times 10^6$	$5.314 \times 10^5$
C (solid, graphite) + $1/2O_2$ (gas) = $CO$ (gas).....		$1.117 \times 10^{24}$	$8.481 \times 10^{23}$	$1.339 \times 10^{19}$	$1.790 \times 10^{16}$	$2.169 \times 10^{14}$	$9.221 \times 10^{12}$	$8.549 \times 10^{11}$	$1.325 \times 10^{11}$	$3.004 \times 10^{10}$	$8.800 \times 10^9$	$3.150 \times 10^9$	$1.311 \times 10^9$	$6.166 \times 10^8$	$3.195 \times 10^8$
C (solid, graphite) + $O_2$ (gas) = $CO_2$ (gas).....		$1.234 \times 10^{61}$	$4.656 \times 10^{58}$	$3.439 \times 10^{41}$	$1.812 \times 10^{34}$	$2.518 \times 10^{24}$	$3.185 \times 10^{19}$	$6.709 \times 10^{15}$	$9.257 \times 10^{12}$	$4.751 \times 10^{10}$	$6.347 \times 10^{18}$	$1.738 \times 10^{17}$	$8.252 \times 10^{15}$	$6.040 \times 10^{14}$	$3.792 \times 10^{13}$
C (solid, graphite) + $2H_2$ (gas) = $CH_4$ (gas).....		$7.916 \times 10^8$	$6.572 \times 10^8$	$3.090 \times 10^5$	$2.672 \times 10^3$	100	8.966	1.411	0.3250	$9.829 \times 10^{-2}$	$3.677 \times 10^{-2}$	$1.608 \times 10^{-2}$	$7.932 \times 10^{-3}$	$4.327 \times 10^{-3}$	$2.554 \times 10^{-3}$

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	-0.37226	+0.41655	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	0.95560	0.60620	0.34312	0.13790	-0.02484	-0.15699	-0.26478	-0.35562	-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	+0.11607	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	+0.45919	1.56218	2.47118	3.23615	3.88982	4.45042	4.94050
Equilibrium constant, $K$															
C (solid, graphite) + $CO_2$ (gas) = $2CO$ (gas).....		$1.012 \times 10^{-21}$	$1.546 \times 10^{-21}$	$5.214 \times 10^{-14}$	$1.768 \times 10^{-9}$	$1.868 \times 10^{-6}$	$2.669 \times 10^{-4}$	$1.098 \times 10^{-2}$	0.1926	1.900	12.20	57.09	$2.083 \times 10^2$	$6.286 \times 10^2$	$1.623 \times 10^3$
C (solid, graphite) + $H_2O$ (gas) = $CO$ (gas) + $H_2$ (gas).....		$1.002 \times 10^{-16}$	$1.387 \times 10^{-16}$	$7.713 \times 10^{-11}$	$2.228 \times 10^{-7}$	$5.059 \times 10^{-5}$	$2.407 \times 10^{-3}$	$4.399 \times 10^{-2}$	0.4244	2.609	11.58	39.77	$1.135 \times 10^2$	$2.770 \times 10^2$	$6.013 \times 10^2$
$CO$ (gas) + $1/2O_2$ (gas) = $CO_2$ (gas).....		$1.106 \times 10^{45}$	$5.492 \times 10^{44}$	$2.568 \times 10^{32}$	$1.013 \times 10^{23}$	$1.161 \times 10^{20}$	$3.453 \times 10^{16}$	$7.848 \times 10^{13}$	$6.930 \times 10^{11}$	$1.582 \times 10^{10}$	$7.210 \times 10^8$	$5.519 \times 10^7$	$6.293 \times 10^6$	$9.810 \times 10^5$	$1.970 \times 10^5$
$CO$ (gas) + $H_2O$ (gas) = $CO_2$ (gas) + $H_2$ (gas).....		$9.926 \times 10^4$	$8.975 \times 10^4$	$1.479 \times 10^3$	$1.260 \times 10^2$	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).....		$1.411 \times 10^{15}$	$1.290 \times 10^{15}$	$4.253 \times 10^{13}$	$6.710 \times 10^{12}$	$2.169 \times 10^{12}$	$1.028 \times 10^{12}$	$6.060 \times 10^{11}$	$4.108 \times 10^{11}$	$3.056 \times 10^{11}$	$2.392 \times 10^{11}$	$1.957 \times 10^{11}$	$1.652 \times 10^{11}$	$1.425 \times 10^{11}$	$1.251 \times 10^{11}$
$CH_4$ (gas) + $CO_2$ (gas) = $2CO$ (gas) + $2H_2$ (gas).....		$1.278 \times 10^{-30}$	$2.348 \times 10^{-30}$	$1.652 \times 10^{-19}$	$6.625 \times 10^{-13}$	$1.868 \times 10^{-8}$	$2.978 \times 10^{-5}$	$7.722 \times 10^{-3}$	0.5929	19.32	$3.316 \times 10^2$	$3.548 \times 10^3$	$2.626 \times 10^4$	$1.452 \times 10^5$	$6.352 \times 10^5$
$CH_4$ (gas) + $H_2O$ (gas) = $CO$ (gas) + $3H_2$ (gas).....		$1.266 \times 10^{-25}$	$2.107 \times 10^{-25}$	$2.447 \times 10^{-16}$	$8.732 \times 10^{-11}$	$5.058 \times 10^{-7}$	$2.687 \times 10^{-4}$	$3.120 \times 10^{-2}$	1.306	26.56	$3.133 \times 10^2$	$2.473 \times 10^3$	$1.428 \times 10^4$	$6.402 \times 10^4$	$2.354 \times 10^5$
$CH_4$ (gas) + $2H_2O$ (gas) = $CO_2$ (gas) + $4H_2$ (gas).....		$1.257 \times 10^{-20}$	$1.891 \times 10^{-20}$	$3.623 \times 10^{-13}$	$1.151 \times 10^{-8}$	$1.369 \times 10^{-5}$	$2.423 \times 10^{-3}$	0.1260	2.879	36.49	$2.959 \times 10^2$	$1.723 \times 10^3$	$7.759 \times 10^3$	$2.821 \times 10^4$	$8.720 \times 10^4$

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  $(F^p - F^0)$  and  $\Delta(F^p - F^0)$  for various pressures and temperatures are given by the relations:

For C (solid, graphite)—

$$(F^p - F^0) = [0.12843 + 7.617 \times 10^{-7}T + 4.848 \times 10^{-10}T^2] \\ [(P-1) - 1.52 \times 10^{-6}(P^2-1) + 1.54 \times 10^{-12}(P^3-1)] \text{ cal/mole,} \quad (36)$$

For C (solid, diamond)—

$$(F^p - F^0) = [0.082777 - 1.505 \times 10^{-7}T + 5.631 \times 10^{-10}T^2] \\ + 3.6224 \times 10^{-13}T^3 [(P-1) - 8.0 \times 10^{-8}(P^2-1) \\ + 4.0 \times 10^{-15}(P^3-1)] \text{ cal/mole,} \quad (37)$$

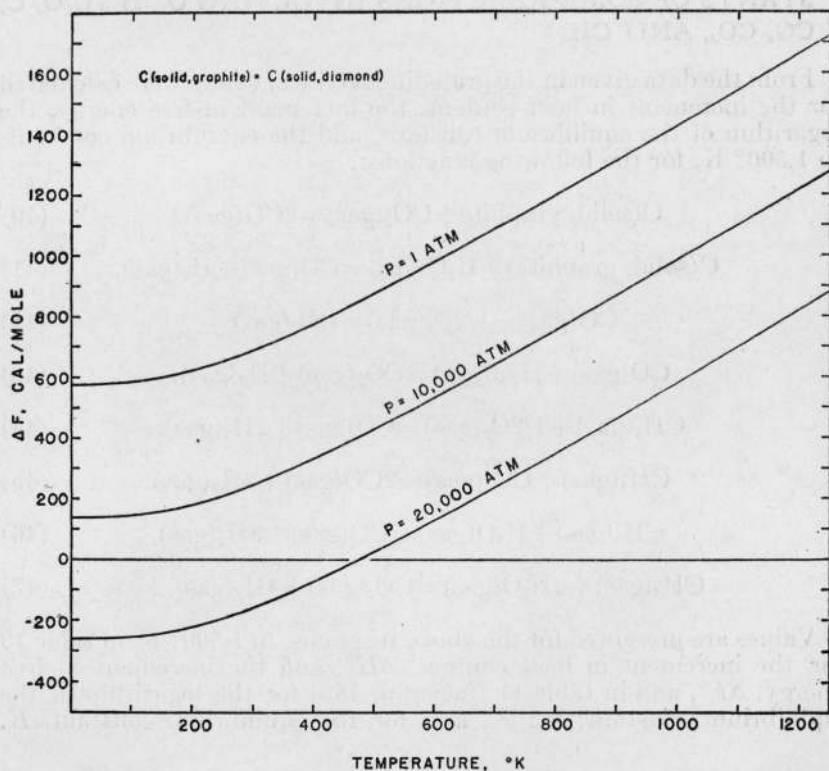
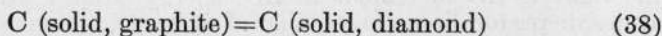


FIGURE 1.—Plot of the free energy change for the transition of graphite into diamond.

The scale of ordinates gives the increment in free energy,  $\Delta F^0$ , 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—



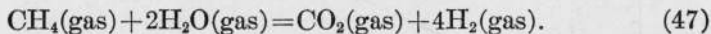
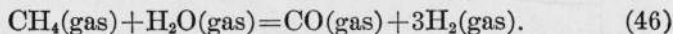
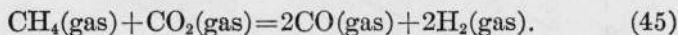
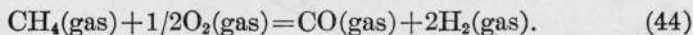
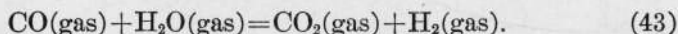
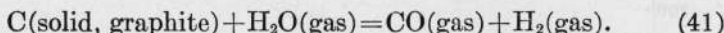
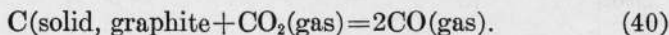
$$\begin{aligned} \Delta(F^p - F^o) = & -[0.045653 + 9.122 \times 10^{-7}T - 7.83 \times 10^{-11}T^2 \\ & - 3.6224 \times 10^{-13}T^3][P - 1] + [1.886 \times 10^{-6} + 1.17 \times 10^{-12}T \\ & + 6.92 \times 10^{-16}T^2 - 2.9 \times 10^{-20}T^3][P^2 - 1] - [1.974 \times 10^{-13} \\ & + 1.174 \times 10^{-18}T + 7.44 \times 10^{-22}T^2 - 1.45 \times 10^{-27}T^3][P^3 - 1] \text{cal/mole.} \end{aligned} \quad (39)$$

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 $\text{O}_2$ , $\text{H}_2$ , $\text{H}_2\text{O}$ , $\text{C}$ , $\text{CO}$ , $\text{CO}_2$ , AND $\text{CH}_4$

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:



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



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

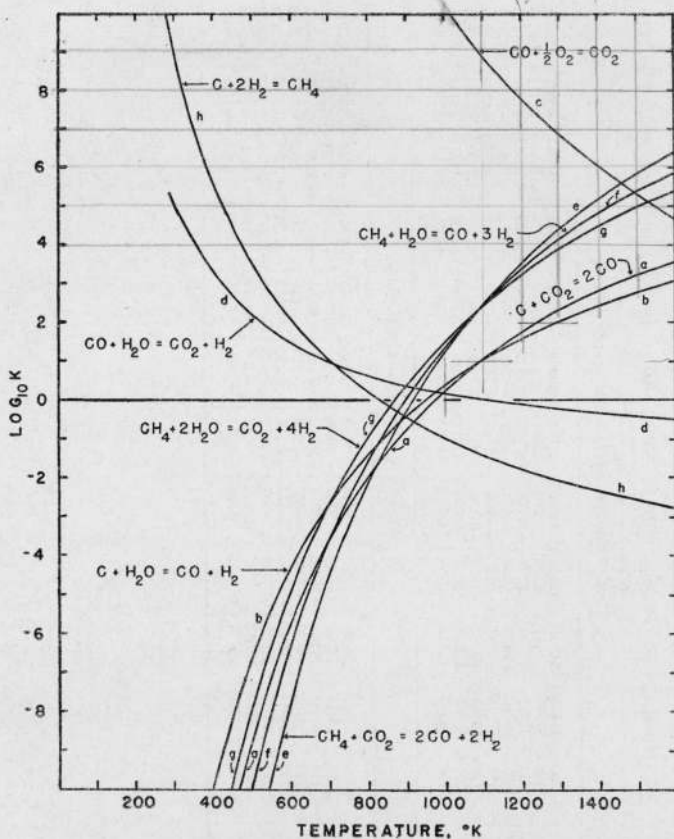


FIGURE 2.—Plot of the logarithm of the equilibrium constant for eight reaction involving  $O_2$ ,  $H_2$ ,  $H_2O$ ,  $C$  (graphite),  $CO$ ,  $CO_2$ , and  $CH_4$ .

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)  $C(\text{solid, graphite}) + CO_2(\text{gas}) = 2CO(\text{gas})$ .
- (b)  $C(\text{solid, graphite}) + H_2O(\text{gas}) = CO(\text{gas}) + H_2(\text{gas})$ .
- (c)  $CO(\text{gas}) + \frac{1}{2}O_2(\text{gas}) = CO_2(\text{gas})$ .
- (d)  $CO(\text{gas}) + H_2O(\text{gas}) = CO_2(\text{gas}) + H_2(\text{gas})$ .
- (e)  $CH_4(\text{gas}) + CO_2(\text{gas}) = 2CO(\text{gas}) + 2H_2(\text{gas})$ .
- (f)  $CH_4(\text{gas}) + H_2O(\text{gas}) = CO(\text{gas}) + 3H_2(\text{gas})$ .
- (g)  $CH_4(\text{gas}) + 2H_2O(\text{gas}) = CO_2(\text{gas}) + 4H_2(\text{gas})$ .
- (h)  $C(\text{solid, graphite}) + 2H_2(\text{gas}) = CH_4(\text{gas})$ .

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