12. The apparent increase in specific heat caused by the dissociation is calculated. Even at temperatures as low as 2000° the effect should be perceptible. The magnitude of the effects found is, according to statements of Seigel, of the right order to account fully for certain anomalies in the experiments of Bjerrum. Therefore, the results of the explosion method, instead of conflicting with the present determinations of the degree of dissociation, may be regarded as additional evidence in their favor.

13. The rate at which hydrogen at very low pressures is dissociated by a tungsten wire at 1200–1500° has been calculated according to the theory and is found to be 8–10 times greater than the *greatest* observed rate at which active hydrogen was deposited on glass surfaces. In view of the marked fatigue effects characteristic of this adsorption of active hydrogen by glass, the agreement is close enough to lend further support to the theory. The quantitative evidence of the dissociation of hydrogen may therefore be said to extend over a temperature range from 1200 to 3500° K., in which the degree of dissociation increases in the ratio 1:170000.

14. Experiments on the heat losses from tungsten wires in mixtures of nitrogen and hydrogen yield results also in accord with the theory. See Table XXI. The diffusion coefficient of hydrogen atoms through nitrogen is found to be

$$D = 2.5\ (T/273)^{3/2}$$

which is in excellent agreement with a value calculated by the kinetic theory.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF SOME CARBON COMPOUNDS.

BY GILBERT N. LEWIS AND MERLE RANDALL.

Received December 15, 1914.

Elementary Forms of Carbon.

Of the numerous known forms of carbon only two, graphite and diamond, appear to be true chemical individuals. Indeed it is possible that substances like coal, charcoal, and coke should be regarded, not as elementary carbon, but as mixtures of hydrocarbons of low hydrogen content. Passing from benzene through naphthalene to more unsaturated compounds of higher molecular weight there seems to be no limit to the ratio between the number of carbon atoms to the number of hydrogen atoms in a hydrocarbon molecule. However, there are certain of the so-called amorphous forms of carbon, such as the one produced by the decomposition of pure carbon monoxide, which must be regarded as pure, but of which the properties vary according to the method of preparation. They may consist of very minute crystals of varying size, but it is more probable that they should be regarded as liquids of enormous viscosity, or even as sponge-like gels, of which the density, heat capacity and other characteristic properties are determined by the conditions under which they are formed.

In determining the difference in free energy of the elementary forms of carbon, it is impossible to proceed as we have in the case of sulfur, since no transition points are known. Schenck and Heller[1] believed that they had discovered, in the equilibrium between carbon, iron, ferrous oxide, and the oxides of carbon, different equilibrium pressure curves for the different modifications of carbon, the pressure being higher with amorphous carbon and diamond than with graphite. Theoretically it is barely conceivable that, by the intervention of a phenomenon analogous to supercooling, true equilibria involving in one case diamond and in another case graphite might be obtained. But it has been shown by Falcke[2] that under the conditions of Schenck and Heller's experiments this certainly is not the case. Pring and Fairlie[3] in their investigation of the equilibrium between carbon, hydrogen, and methane obtained in all cases a larger proportion of methane with amorphous carbon than with graphite, but on standing, with amorphous carbon, the percentage of methane diminished as the carbon became graphitized, until the conditions obtained with pure graphite were established. It is possible that in the early stages of their experiments with amorphous carbon there was a close approach to equilibrium between this substance and the gaseous mixture. Aside from these investigations we have no chemical data which enable us to calculate the difference in free energy of the forms of carbon.

In order, therefore, to determine the difference in free energy between the two modifications of definite properties, graphite and diamond, we shall make use of a method which we have not hitherto employed in these calculations. Numerous attempts have been made to calculate free energy changes from thermal data alone, notably by Nernst and his collaborators. For the most part these calculations have involved assumptions of only approximate validity, such as Trouton's rule or the Nernst theorem concerning the so-called chemical constants. But one generalization has been developed which appears to possess universal validity. It was first clearly stated by Planck, and may be called the Second Law of Entropy. We may express this law as follows: *Every substance*[4] *possesses zero entropy at the absolute zero of temperature.*

---

[1] Schenck and Heller, *Ber.*, 38, 2139 (1905).

[2] Falcke, *Ber.*, 46, 743 (1913).

[3] Pring and Fairlie, *J. Chem. Soc.*, 101, 91 (1912).

[4] This law is true of every *actual* substance. The entropy of an ideal gas, that is, of a gas at zero pressure, is indeterminate at the absolute zero.

Let us consider one mol. of a substance, of which the heat capacity at constant pressure is C_p. Now if it be cooled at constant pressure from the temperature T to the absolute zero, the total diminution in entropy is $S_T - S_0 = \int_0^T \frac{C_p}{T}\,dT$. According to the law just stated $S_0 = 0$. Hence

$$S_T = \int_0^T \frac{C_p}{T}\,dT = \int_0^T C_p\,d\ln T. \qquad (1)$$

Now in any chemical reaction $aA + bB + \ldots\ldots = cC + dD + \ldots\ldots$, if S_A is the molal entropy of A, etc.,

$$\Delta S = cS_C + dS_D + \ldots\ldots - aS_A - bS_B - \ldots\ldots$$

If the heat capacity of each substance, at the pressure at which it occurs in the reaction, is known as a function of the temperature, down to the absolute zero, we may calculate the entropy of each substance at the temperature in question and thus obtain ΔS for the reaction. But we also have the thermodynamic relation,

$$T\Delta S = \Delta H - \Delta F; \qquad (2)$$

hence if the heat of reaction and the heat capacity curves of the several substances are accurately known we may determine exactly the value of ΔF.

The calculation of the entropy from the heat capacity curves can be carried out with a high degree of accuracy in many cases, owing to the fact that, since the heat capacity falls so rapidly with diminishing temperature, the range of very low temperatures, where accurate measurements are most difficult, contributes almost nothing to the entropy. According to the theory of Debye[1] the heat capacity of crystalline substances belonging to the regular system is proportional to the cube of the temperature, and Lewis and Adams[2] have shown that it is probable that this is true of all substances at very low temperatures. In the range of validity of this law it follows from (1) that

$$S = 1/3\ C_p. \qquad (3)$$

At higher temperatures we might obtain the integral of Equation 1 by the use of one of the various heat capacity equations that have been proposed. But a far simpler method, which is perfectly general and involves no assumptions, consists in plotting C_p as ordinate and ln T as abscissa and determining the area under the curve up to the temperature in question. We shall illustrate this method in determining the difference in free energy between graphite and diamond.

$C_G = C_D$.—Since graphite is not only the stable form, but is also the

---

[1] Debye, *Ann. Physik.*, 39, 789 (1912).

[2] Lewis and Adams, *Physic. Rev.*, [2] 4, 331 (1914).

one which has been used in high temperature equilibrium measurements, we shall consider it the standard state of elementary carbon. The most reliable measurements of the heat capacity of diamond and of graphite seem to be those of Weber[1] at high temperatures, and of Nernst[2] of and Koerpf[3] at low temperatures. We have attempted in Fig. 1 to give the most probable curves on the basis of existing data for the heat capacities of the two substances.[4] The ordinates are the values of C_p, the molal heat capacity, in calories per degree, and the abscissas are the common logarithms of T. It is evident that the area under the diamond curve below the temperature

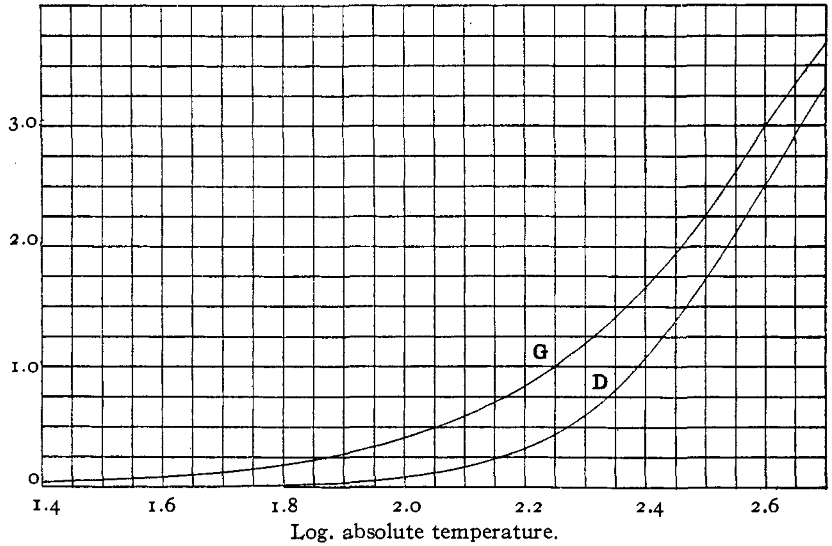

Fig. 1.—Heat Capacity of Diamond and Graphite.

---

[1] Weber, *Phil. Mag.*, [4] 49, 161, 276 (1875); *Ann. Physik. Chem.*, [2] 154, 367 (1875).

[2] Nernst, *Ann. Physik.*, [4] 36, 395 (1911).

[3] Koref, *Ibid.*, [4] 36, 49 (1911).

[4] At the highest temperatures the results of Weber were obtained by comparing diamond and graphite with platinum dropped from the same temperature into a double calorimeter. His furnace temperatures were estimated from the best data then existing for the specific heat of platinum. Those values now appear to be erroneous and we have, therefore, recalculated Weber's results at the three high temperatures where this method was employed, using White's formula for the specific heat of platinum, *Am. J. Sci.*, [4] 28, 334 (1909). We thus find for C_p (graphite) 4.85 at 950° A, 4.88 at 1150°, 4.95 at 1320°; and C_p (diamond) 4.80 at 913° A, 4.88 at 1124°, 4.82 at 1331°. It is to be noted, however, that Weber's results at lower temperatures as well as the theoretical curve obtained for diamond as a substance in the regular crystalline system, point to values nearer to those originally given by Weber, and it is possible that through some compensating error his results as originally given are more accurate than our recalculated values.

corresponding to $\log T = 1.4$ is entirely negligible. At this low temperature the graphite has not yet reached the point where it obeys the T^3 law, but we estimate that the entropy at this temperature is about 0.03, an almost negligible amount. By counting squares up to $T = 298.1$, $\log T = 2.474$, we find for the area under the graphite curve 47.80 of the squares shown in the figure. Owing to the scale of the plot, and to the fact that we are using common logarithms, we must multiply this figure by 2.303/80 and thus obtain 1.37; adding 0.03 we find for graphite $S_{298} = 1.40$. Similarly we find for diamond $S_{298} = 0.60$. Hence we find for our reaction

$$\Delta S_{298} = -0.80 \text{ cal. per degree.} \qquad (4)$$

The older determinations of the heats of combustion of graphite and diamond were too inaccurate to give ΔH, but the recent very careful work of Roth and Wallasch[1] indicates that the heat of combustion of diamond is larger than that of graphite by 280 cal. Thus $\Delta H_{298} = 280$. In general $\Delta F = \Delta H - T\Delta S$, hence

$$C_G = C_D;\ \Delta F^\circ_{298} = 280 + 298 \times 0.80 = 520. \qquad (5)$$

Another form of our fundamental free energy equation is

$$d(\Delta F)/dT = -\Delta S.$$

If the statement of Weber is correct that at higher temperatures the heat capacity of diamond approaches but never exceeds that of graphite, then ΔS is always negative, and ΔF remains positive at all temperatures, increasing with increasing temperatures. At all temperatures, therefore, graphite is more stable than diamond at atmospheric pressure. In the formation of diamond, then, we may have another illustration of the frequent phenomenon that an unstable modification appears before the stable one has an opportunity to form. But if diamond is formed at very high pressures it may be the stable form, and if the value given above for ΔF°_{298} is correct we may calculate the transition pressure. Taking the volume per gram atom of diamond as 3.4 cc., and of graphite as 5.5 cc., the increase in free energy of either substance in compressiom from 1 atmos. to p atmos. is (neglecting the compressibility) $\Delta F = v\,(p - 1)$.[2] Substituting the atomic volumes and converting from cubic centimeter—atmospheres to calories, and using the above value of ΔF°_{298} we find that at room temperature diamond will be more stable than graphite at pressures above 10,000 atmos. At higher pressures, assuming any reasonable values for the coefficient of expansion, the transition pressure will increase rather than diminish.

Oxides of Carbon.

$C + CO_2 = 2CO$.—The equilibrium between carbon, carbon monoxide and carbon dioxide has been studied by several investigators. The work

---

[1] Roth and Wallasch, *Ber.*, 46, 896 (1913).

[2] Lewis, "Free Energy of Chemical Substances," Equation 11, THIS JOURNAL, 35, 16 (1913).

of Boudouard[1] gave the order of magnitude of the equilibrium constant and its change with the temperature, but his work has been superseded by the very careful measurements of Rhead and Wheeler.[2] In their experiments, wood charcoal was used, which was treated with chlorine at 1000° for 24 hrs., and later with other gases for several days at the same temperature, so that we may assume that their carbon was, at least on the surface, in the form of graphite. The heat capacity of an element at temperatures below the range of validity of the law of Dulong and Petit cannot be represented by a simple algebraic expression. We find, however, that the heat capacity curve of graphite, between 0° C. and 2000° C. may be fitted with sufficient accuracy for our purpose by the quadratic equation,

$$C_G;\ C_p = 1.1 + 0.0048T - 0.0000012T^2. \qquad (6)$$

From our previous paper,[3]

$$CO_2;\ C_p = 7.0 + 0.0071T - 0.00000186T^2.$$

$$CO;\ C_p = 6.5 + 0.0010T.$$

Hence

$$\Delta\Gamma = 4.9 - 0.0099T + 0.00000306T^2.$$

$$\Delta H = \Delta H_0 + 4.9T - 0.00495T^2 + 0.00000102T^3.$$

$$\Delta F^\circ = \Delta H_0 - 4.9T \ln T + 0.00495T^2 - 0.00000051T^3 + IT.$$

The value of ΔH_{291} can be obtained from the heat of formation of CO_2 from graphite which is given by Roth and Wallasch[4] as 94250, and from the heat of combustion of CO for which Berthelot gives 68300 and Thomsen 67960, the mean being 68100. Combining these two values $\Delta H_{291} = 41950$, and from the above equation $\Delta H_0 = 40910$.

The values of I at the various temperatures of Rhead and Wheeler's measurements can now be obtained, and are given in Table I, in which

TABLE I.

T.	% CO.	% CO_2.	K.	ΔF°.	I.
1123	93.77	6.23	14.11	—5900	—12.16
1173	97.78	2.22	43.07	—8760	—12.73
1223	98.68	1.32	73.77	—11190	—12.43
1273	99.41	0.59	167.5	—12940	—12.72
1323	99.63	0.37	268.3	—14680	—12.46
1373	99.85	0.15	664.7	—17720	—13.15
1473	99.94	0.06	1665	—21690	—12.95
				Average,	—12.66

---

[1] Boudouard, *Compt. rend.*, 130, 132 (1900).

[2] Rhead and Wheeler, *J. Chem. Soc.*, 97, 2178 (1910). In the recent work of Clement, U. S. Bureau of Mines, *Bull.* 17 (1911), the rate of this reaction was chiefly studied. His estimate of the equilibrium constant is evidently erroneous, owing to the fact that his experiments were of too short duration to permit the attainment of equilibrium conditions.

[3] Lewis and Randall, THIS JOURNAL, 34, 1128 (1912).

[4] Roth and Wallasch, *loc. cit.*

the first column gives the absolute temperatures, the next two the percentages of CO and of CO_2 in the equilibrium mixture at atmospheric pressure, the fourth the equilibrium constant, the fifth $\Delta F^\circ = - R'T \ln K$, and the sixth the values of I obtained from the several values of ΔF°.

The values of I show excellent constancy, and considering the difficulties of the experiment, this must be regarded as one of the most satisfactory investigations of high temperature equilibrium. Using the mean value of I we have

$$C_G + CO_2 = 2CO; \ \Delta F^\circ_{298} = 29240$$

$$\Delta F^\circ = 40910 - 4.9T \ln T + 0.00495T^2 - 0.000000051T^3 - 12.66T. \quad (7)$$

$CO_2 + H_2 = CO + H_2O(g)$.—This reaction, known as the water gas reaction, has been the subject of numerous investigations. The formulas for the heat capacities of these four gases are given in our previous paper[1] from which we find

$$\Delta\Gamma = 1.81 - 0.0089T + 0.00000408T^2.$$

For the formation of water vapor from its elements, $\Delta H_0 = - 57410$,[2] and for the formation of carbon dioxide from carbon monoxide and oxygen, $\Delta H_0 = - 67510$ as we show in the next reaction. Hence for the water gas reaction $\Delta H_0 = 10100$ and

$$\Delta F^\circ = 10100 - 1.81T \ln T + 0.00445T^2 - 0.00000068T^3 - 0.54T. \quad (8)$$

The value of $I = - 0.54$ is obtained from the important determinations of the equilibrium in this reaction by Hahn[3] and by Haber and Richardt.[4] Their results are summarized in Tables II and III. The first row gives the absolute temperature of the measurements, the second the equilibrium constant, and the third the value of I calculated therefrom.

TABLE II (HAHN).

T....	959	1059	1159	1209	1278	1359	1478	1678
K....	0.534	0.840	1.197	1.571	1.620	1.960	2.126	2.490
I.....	—0.59	—0.53	—0.56	—0.79	—0.49	—0.50	—0.23	0.06

TABLE III (HABER AND RICHARDT).

T.....	1503	1528	1538	1582	1597	1643	1768	1783	1797	1824
K.....	3.05	2.68	2.85	2.72	2.93	3.26	3.83	3.66	3.86	3.56
I......	—0.65	—0.51	—0.58	—0.37	—0.47	—0.64	—0.61	—0.47	—0.55	—0.32

In Hahn's work the gases were allowed to stream by a catalyzer and were rapidly cooled, but, as pointed out by Haber[5] in his critical résumé of this equilibrium, the discrepancy between Hahn's measurements at high and low temperatures is due to the difficulty in cooling the mixture from a high temperature rapidly enough to prevent the continuance of the re-

---

[1] Lewis and Randall, THIS JOURNAL, 34, 1128 (1912).

[2] Lewis and Randall, *Ibid.*, 36, 1981 (1914).

[3] Hahn, *Z. physik. Chem.*, 44, 513 (1903); 48, 735 (1904).

[4] Haber and Richardt, *Z. anorg. Chem.*, 38, 5 (1904).

[5] Haber, "Thermodynamics of Technical Gas Reactions."

action. This criticism apparently does not hold for Hahn's lower temperatures and we may take from his first three measurements $I = -0.56$. The measurements of Haber and Richardt were obtained by a study of the temperature and composition of the gases in the free flame. The agreement of the values of I with one another, and with those of Hahn at low temperature, not only give us great confidence in the reliability of the experimental results, but also in the equations which we have chosen to express the heat capacities of the several gases involved. The discussion given in Haber's book shows how extremely difficult it is to interpret high temperature equilibrium measurements when there is any serious doubt concerning the true heat capacity values. We have chosen as a final mean $I = -0.54$, hence

$$H_2 + CO_2 = H_2O(g) + CO: \quad \Delta F^\circ_{298} = 7240. \qquad (9)$$

$CO + {}^1/_2O_2 = CO_2$.—Another important check upon the calculation just made is furnished by the study of the dissociation of carbon dioxide, for by combining (8) with Equation 56 of our paper on oxygen and hydrogen compounds,

$$\begin{array}{lll} CO + H_2O(g) & = H_2 + CO_2; & \Delta F^\circ_{298} = -\ 7240 \\ H_2 + {}^1/_2O_2 & = H_2O(g) \quad ; & \Delta F^\circ_{298} = -\ 54567 \\ \hline CO + {}^1/_2O_2 & = CO_2 \qquad ; & \Delta F^\circ_{298} = -\ 61807. \end{array}$$

We may now proceed to calculate the free energy of this reaction from direct measurements of the dissociation of carbon dioxide. The heat capacity values we shall take once more from our paper on specific heats and find $\Delta\Gamma = -2.75 + 0.0056T - 0.00000186T^2$. We have already found $\Delta H_{291} = -68100$, whence $\Delta H_0 = -67510$ and

$$\Delta F^\circ = -67510 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + IT.$$

The calculation of I from the experiments of Nernst and von Wartenberg,[1] Langmuir[2] and Löwenstein[3] is shown in Table IV. The first column gives the absolute temperature of the measurements, the second

TABLE IV.

T.	% dissociation.	K.	I.	
1395	0.0142	837000	4.67	Langmuir
1400	0.015	781000	4.61	Nernst and von Wartenberg
1443	0.025	358000	4.76	Langmuir
1478	0.032	247000	4.39	Nernst and von Wartenberg
1481	0.028	295000	3.94	Langmuir
1498	0.047	138000	4.89	Langmuir
1565	0.064	87300	4.91	Langmuir
1823	0.4	5600	3.28	Löwenstein

---

[1] Nernst and von Wartenberg, *Z. physik. Chem.*, 56, 548 (1906).

[2] Langmuir, THIS JOURNAL, 28, 1357 (1906).

[3] Löwenstein, *Z. physik. Chem.*, 54, 707 (1905).

the percentage dissociation of carbon dioxide at atmospheric pressure, the third the equilibrium constant $p_{CO_2}/(p_{CO}p_{O_2}^{1/2})$, the fourth the value of I, and the fifth the author.

The mean of the several values of I is 4.43, or 4.69 if we exclude the uncertain value of Löwenstein and the one exceptionally low value of Langmuir. On the other hand by direct subtraction of Equation 8 for the water gas reaction from Equation 56 of our previous paper for the free energy of formation of water vapor we find I = 4.26. The agreement is very satisfactory. We shall give greater weight to the water gas reaction which was studied at lower temperatures and choose I = 4.30 as the final value, whence

$$CO + {}^1/_2O_2 = CO_2; \quad \Delta F^\circ_{298} = -61800.$$

$$\Delta F^\circ = -67510 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + 4.30T. \quad (10)$$

$\mathbf{C_G + {}^1/_2O_2 = CO}$.—Adding Equations 7 and 10 gives

$$\Delta F^\circ = -26600 - 2.15T \ln T + 0.00215T^2 - 0.0000002T^3 - 8.36T. \quad (11)$$

$$\Delta F^\circ_{298} = -32560.$$

$\mathbf{C_G + O_2 = CO_2}$.—Adding Equations 10 and 11,

$$\Delta F^\circ = -94110 + 0.60T \ln T - 0.00065T^2 + 0.00000011T^3 - 4.06T. \quad (12)$$

$$\Delta F^\circ_{298} = -94360.$$

Carbonic Acid and Its Ions.

$\mathbf{CO_2 + H_2O(l) = H_2CO_3(aq)}$.[1]—The solubility of CO_2 in water at 25° at a partial pressure of 1 atmos. is 0.0338 mols per liter according to the entirely concordant measurements of Bohr and Bock[2] and of Just.[3] Hence

$$\Delta F^\circ_{298} = -R'T \ln 0.0338 = 2010. \quad (13)$$

$\mathbf{H_2 + C_G + {}^3/_2O_2 = H_2CO_3(aq.)}$. — Adding Equations 12, 13, and Equation 54 of our previous paper,

$$\begin{array}{lll}
C_G + O_2 = CO_2 & ; \ \Delta F^\circ_{298} = - & 94360 \\
CO_2 + H_2O = H_2CO_3(aq.) & ; \ \Delta F^\circ_{298} = & 2010 \\
H_2 + {}^1/_2O_2 = H_2O(l) & ; \ \Delta F^\circ_{298} = - & 56620 \\
\hline
\end{array}$$

$$H_2 + C_G + {}^3/_2O_2 = H_2CO_3(aq.); \quad \Delta F^\circ_{298} = -148970 \quad (14)$$

$\mathbf{H_2CO_3(aq.) = H^+ + HCO_3^-}$.—Walker and Cormack[4] found for the first dissociation constant of carbonic acid $K_{291} = 3.04 \times 10^{-7}$. The heat of this reaction is the heat of mixture of 1 mol H_2CO_3 and 1 mol NaOH, less the heat of neutralization of 1 equivalent of a strong acid. From

---

[1] Of course we make no assumption that the carbon dioxide dissolved in water is all in the form of H_2CO_3. For the purpose of the thermodynamic calculations in which we are engaged it is immaterial whether the substance is all H_2CO_3, or in part CO_2 or higher hydrates than H_2CO_3.

[2] Bohr and Bock, *Ann. Physik*, [3] **44**, 318 (1891).

[3] Just, *Z. physik. Chem.*, **37**, 342 (1901).

[4] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

Thomsen's measurements $\Delta H = 2700$, and, applying the van't Hoff formula, $K_{298} = 3.39 \times 10^{-7}$. Hence

$$\Delta F^\circ_{298} = 8830. \tag{15}$$

$^1/_2H_2 + C_G + {}^3/_2O_2 + \ominus = HCO_3^-$.—Combining Equations 14, 15, and Equation 9 of our previous paper,

$$\begin{array}{lll}
H_2 + C_G + {}^3/_2O_2 = H_2CO_3(aq.) & ; & \Delta F^\circ_{298} = -\ 148970 \\
H_2CO_3(aq.) \qquad\quad = H^+ + HCO_3^- & ; & \Delta F^\circ_{298} = \qquad 8830 \\
H^+ + \ominus \qquad\qquad\ \ = {}^1/_2H^2 & ; & \Delta F^\circ_{298} = \qquad\quad 0 \\
\hline
\end{array}$$

$$^1/_2H_2 + C_G + {}^3/_2O_2 + \ominus = HCO_3^-;\ \Delta F^\circ_{298} = -\ 140140 \tag{16}$$

$HCO_3^- = H^+ + CO_3^{--}$.—The second dissociation constant of carbonic acid has been the subject of investigations by Bodländer,[1] McCoy,[2] and Auerbach and Pick.[3] The uncertainty in this constant seems to be due not so much to the experiments as to the difficulty of interpreting them. We know very little about the concentration of the ion $NaCO_3^-$ or about the concentration and activity of CO_3^{--} in mixtures of sodium carbonate and acid carbonate. McCoy determined the ratio $\frac{(\Sigma NaHCO_3)^2}{(\Sigma H_2CO_3)(\Sigma Na_2CO_3)}$ in solutions M, $0.3M$, and $0.1M$ with respect to $NaHCO_3$, and found 3120, 4460, and 5290, respectively. By a rough extrapolation from these figures we find 6300 at high dilution, where the two salts may be regarded as completely dissociated, and the quotient becomes $\frac{(HCO_3^-)^2}{(H_2CO_3)(CO_3^{--})}$. Dividing by this quotient the first dissociation constant of carbonic acid given above we find $K_{298} = (H^+)(CO_3^{--})/(HCO_3^-) = 5.4 \times 10^{-11}$ as the second dissociation constant of carbonic acid, whence

$$\Delta F^\circ_{298} = 14010. \tag{17}$$

$C_G + {}^3/_2O_2 + 2\ominus = CO_3^{--}$.—Using once more the fact that the free energy of hydrogen ion is taken as zero, and combining Equations 16 and 17,

$$\Delta F^\circ_{298} = -\ 126130. \tag{18}$$

Methane.

$C_G + 2H_2 = CH_4$.—Of all the hydrocarbons the only one for which we have data reliable enough to warrant the present calculation of the free energy is methane.

The specific heat of methane has been determined only through a small range of temperatures. Regnault found $C_p = 9.5$ at about 108°. As might be expected, this is a somewhat higher value than that given by the

---

[1] Bodländer, *Z. physik. Chem.*, **35**, 23 (1900).

[2] McCoy, *Am. Chem. J.*, **29**, 437 (1903).

[3] Auerbach and Pick, *Arb. Kais. Gesundh.*, **38**, 243 (1911).

equation for ammonia. We will modify that equation slightly, therefore, and write

$$CH_4; \quad C_p = 7.5 + 0.005T. \qquad (19)$$

Combining this with the equations already given for hydrogen and graphite, $\Delta\Gamma = -6.6 - 0.0016T + 0.0000012T^2$.

The heat of combustion of methane to form gaseous CO_2 and liquid H_2O is 212400 according to Thomsen, and 212800 according to Berthelot, mean 212600. The heat of formation of liquid water we have shown in a previous paper to be 68470 at 0° C., or 68330 at 18°. Using the heat of combustion of graphite, which we have already taken from the work of Roth and Wallasch, we find for the formation of methane from its elements $\Delta H_{291} = -18300$, and from the equation for $\Delta\Gamma$, $\Delta H_0 = -16300$, and $\Delta F^\circ = -16300 + 6.6T \ln T + 0.0008T^2 - 0.0000002T^3 + IT$. Measurements of the equilibrium in this reaction were made by Mayer and Altmayer[1] but we shall consider chiefly the far more extensive measurements recently made by Pring and Fairlie.[2] These authors obtained a higher yield of methane from amorphous carbon than from graphite, but in the latter case a true equilibrium was reached, whereas in the former the equilibrium continually changed owing to the gradual transition from amorphous carbon to graphite. The ultimate equilibrium was the same as that obtained directly from graphite. We shall give in Table V the various results obtained by Pring and Fairlie without distinguishing between the different varieties of graphite which they used. The first column shows the absolute temperature, the second the equilibrium constant $p_{CH_4}/p^2_{H_2}$, and the third the corresponding value of I. The first value given represents the average of the measurements of Mayer and Altmayer at 823° A with amorphous charcoal, which was covered with a catalyzer of nickel or cobalt and was presumably graphitized in part.

TABLE V.

T.	K.	I.
(823)	(0.64)	(—24.2)
1473	0.00244	—25.9
1548	0.00147	—25.8
1573	0.00146	—26.0
1573	0.00158	—26.2
1648	0.00100	—26.1
1648	0.00117	—26.4
1673	0.00103	—26.4
1673	0.00089	—26.1
1673	0.00089	—26.1
1723	0.00075	—26.1
1773	0.00077	—26.7
1848	0.00062	—27.0

There is evidently a slight trend of I with the temperature. This may be

---

[1] Mayer and Altmayer, *Ber.*, 40, 2134 (1907).

[2] Pring and Fairlie, *J. Chem. Soc.*, 101, 91 (1912). In this paper and in previous papers by the same authors the equilibrium conditions are investigated in the formation, not only of methane, but of ethylene and acetylene. However, we have regarded the experimental data, in the case of the latter hydrocarbons, as too uncertain to make complete free energy calculations desirable at present.

due to an error in the equation assumed for the heat capacity of methane but it may also be an experimental error, the possibility of which the authors themselves have pointed out, namely, an excessive yield of methane at high temperatures owing to the indirect formation of methane, during the rapid cooling of the gas for analysis, from other hydrocarbons which may be present at high temperatures. In either case it would be advisable to give a little more weight to the values at low temperatures and we may take I = 26.0. Hence

$$C_G + 2H_2 = CH_4; \quad \Delta F^\circ_{298} = -12800.$$

$$\Delta F = -16300 + 6.6T \ln T + 0.0008T^2 - 0.0000002T^3 - 26.0T. \quad (20)$$

Carbon Oxychloride.

$CO + Cl_2 = COCl_2(g)$.—In the absence of any reliable measurements of the heat capacity of phosgene we may assume it to be the same as that of ammonia. With the aid of the equations of CO and Cl_2 previously used $\Delta\Gamma = -5.5 - 0.0008T$. Between the values of the heat of this reaction obtained by Thomsen and Berthelot there is a great discrepancy. Thomsen obtains 27000 cal. and Berthelot 19000, which give, respectively, $\Delta H_0 = -25000$; $\Delta H_0 = -17000$. The value of Berthelot seems to be the more reliable and is in agreement with one calculated from the equilibrium measurements of Bodenstein and Dunant[1] which we are about to discuss. We shall take $\Delta H_0 = -18000$, and

$$\Delta F^\circ = -18000 + 5.5T \ln T + 0.0004T^2 - 14.1T. \quad (21)$$

The value of I is obtained from determinations by Bodenstein and Dunant of the dissociation of $COCl_2$ at the three temperatures given in Table VI. From the value of I, $\Delta F^\circ_{298} = -12820$.

TABLE VI.

T.	% dissociation.	K.	I.
776	67	1.227	—14.1
826	80	0.560	—14.3
876	91	0.208	—14.0

$C_G + {}^1/_2O_2 + Cl_2 = COCl_2(g)$.—Combining Equations 11 and 21 gives $\Delta F^\circ_{298} = -45380$, and

$$\Delta F = -44600 + 3.35T \ln T + 0.00255T^2 - 0.0000002T^3 - 22.46T. \quad (22)$$

We wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the various compounds of carbon considered in this paper.

---

[1] Bodenstein and Dunant, *Z. physik. Chem.*, 61, 437 (1907).

TABLE VII.

Substance.	F°_{298}.	Equation.	Substance.	F°_{298}.	Equation.
Diamond	520	5	HCO_3^-	—140140	16
$CO(g)$	—32560	11	CO_3^{--}	—126130	18
$CO_2(g)$	—94360	12	CH_4	—12800	20
H_2CO_3 (aq.)	—148970	14	$COCl_2$	--45380	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

COMPRESSIBILITIES OF MERCURY, COPPER, LEAD, MOLYBDENUM, TANTALUM, TUNGSTEN AND SILVER BROMIDE.

BY THEODORE W. RICHARDS AND EDWARD P. BARTLETT.

Received January 6, 1915.

The compressibilities of the elements are data of great interest, in common with all the other properties of these fundamental substances. Until recently, however, they received but little attention. Six years ago, for the first time, results for a large number of elements, consistently determined by a new and adequate method, were available.[1] From these results it became clear that compressibilities, like many other properties of the elements, are highly periodic in their nature as referred to the progressively increasing atomic weights. Since that time much interest has been taken in the subject, and Bridgman,[2] at the Jefferson Physical Laboratory at Harvard University, and Grüneisen,[3] at the Physikalisch-technische Reichanstalt in Berlin, have both thrown further light upon it. In the main, these results have confirmed and amplified the earlier Harvard results, but there remain two or three points of difference to be explained, and, moreover, it seemed highly desirable to extend the list of elements. Hence the present investigation was undertaken with both of these aims in view. The method employed was precisely that used in preceding investigations,[4] except that in our most accurate work the piezometer was made of soft steel instead of glass. For the details the reader is referred to earlier publications.

In brief, the method consisted in the determination of the difference between the compressibility of each substance in question and that of mercury, which was itself determined by reference to iron. The linear compressibility of iron has been absolutely determined by Bridgman. The piezometer used in the present investigation consisted of a cylindrical vessel of glass or soft steel filled with mercury, being so arranged that the

---

[1] Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst. Wash.*, No. 76 (1907); *Z. physik. Chem.*, 61, 77, 183 (1908); THIS JOURNAL, 31, 154 (1909).

[2] Bridgman, *Proc. Amer. Acad.*, 47, 347 (1911).

[3] *Ann. phys.*, 25, 825 (1908); 33, 1239 (1910).

[4] See for example THIS JOURNAL, 34, 971 (1912); see also Stähler's "Handbuch der Arbeitsmethoden in der anorganischen Chemie," Vol. III, p. 246 (1912).