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The Free Energy of Steam and of Carbon Dioxide

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The free energy of steam is computed from the moments of inertia determined by Mecke and Baumann, and from the fundamental frequencies of Mecke and of Plyler, for temperatures up to 3000°K. From these numbers, the free energy of carbon dioxide (computed from Martin and Barker's data), the known free energies of carbon monoxide and hydrogen, and the thermal data of Rossini, the equilibrium constant for the water-gas reaction is obtained. The calculated equilibrium constants agree with the best experimental values for the temperature range 700°–1259°K within the limits of error of the experiments. The equilibrium constant for the dissociation of steam into

diatomic oxygen and hydrogen is also tabulated, but an unambiguous comparison with experiment is not possible for this reaction, since steam may also dissociate into hydroxyl and hydrogen and the data necessary for a reliable calculation of the hydroxyl dissociation are not available. A calculation for the producer-gas equilibrium predicts greater dissociation of the CO₂ into CO and graphite than is found by experiment; this discrepancy can be accounted for if graphite is assumed to have a "zero point" entropy in excess of that given by the third law of thermodynamics.

IN a recent paper¹ the equilibrium constant for the water-gas reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ was calculated from spectroscopic data. In that calculation, Mecke's older values² for the moments of inertia of the water molecule (0.98, 1.80, 2.80×10^{-40}) were used and the resulting $R \ln K$ were in general about 0.2 calory per degree less than the experimental values of Neumann and Koehler.³ Since that time, two independent determinations of the rotational constants have appeared, the first by Lueg and Hedfeld⁴ and the second by Mecke and Baumann,⁵ and as a result a more accurate calculation is now possible for reactions involving steam.

Lueg and Hedfeld give for the moments of inertia $A = 0.97$, $B = 2.13$, $C = 3.07 \times 10^{-40}$, while Mecke and Baumann give $A = 1.09$, $B = 1.907$, $C = 2.985 \times 10^{-40}$. In the calculation of the "free energy" and entropy for moderate and high temperatures, it is the effective moment of inertia $\bar{I} = (ABC)^{\frac{1}{3}}$ which is the significant quantity, and either set of rotational constants leads to approximately the same result. In the follow-

ing calculations, the values used were $B = 1.907 \times 10^{-40}$, $C = 2.985 \times 10^{-40}$, $A = C - B = 1.078 \times 10^{-40}$, giving $\bar{I} = 1.831 \times 10^{-40}$; had Lueg and Hedfeld's moments of inertia been selected, \bar{I} would have been 1.851×10^{-40} , and the entropy and $-(F^0 - E_0^0)/T$ (Table I) would have been 0.033 greater throughout.

As far as the vibrational contributions to the entropy and free energy are concerned, there is still an uncertainty as to the third fundamental frequency of the water molecule. Mecke⁶ gives $\delta = 1600$, $\nu(\pi) = 3740$, $\nu(\sigma) = 3850 \text{ cm}^{-1}$; while Plyler⁷ gives $\delta = 1597$, $\nu(\pi) = 3742$, $\nu(\sigma) = 5309 \text{ cm}^{-1}$. For any temperature less than 1000°K, either assignment leads to the same value of $-(F^0 - E_0^0)/T$ within 0.01 cal./deg.; for temperatures greater than 1000°, however, the contribution of $\nu(\sigma)$ becomes appreciable, and for this reason $-(F^0 - E_0^0)/T$ in the range 1100°–3000° has been computed both for Plyler's and Mecke's frequencies, the values based on the latter being indicated by the star.

The free energy is obtained from the familiar relation

$$\begin{aligned} &-(F^0 - E_0^0)/T \\ &= -7.267 + 5R/2 \cdot \ln T + 3R/2 \cdot \ln 18.016 \\ &\quad + 3R/2 \cdot \ln 8\pi^{7/3} \bar{I} kT/h^2 - R \cdot \ln 2 + R \cdot \ln Q_v, \end{aligned}$$

¹ Gordon and Barnes, *J. Phys. Chem.* **36**, 1143 (1932).

² Mecke, *Trans. Faraday Soc.* **26**, 214 (1930).

³ Neumann and Koehler, *Zeits. f. Elektrochemie* **34**, 218 (1928).

⁴ Lueg and Hedfeld, *Zeits. f. Physik* **75**, 512 (1932).

⁵ Mecke and Baumann, *Phys. Zeits.* **33**, 833 (1932).

⁶ Mecke, *Zeits. f. Physik* **64**, 173 (1930).

⁷ Plyler, *Phys. Rev.* **39**, 77 (1932).

TABLE I. *The free energy of steam.*

$T^{\circ}\text{K}$	298.1	300	400	500	600	700
$-(F^0 - E_0^0)/T$	37.226	37.28	39.57	41.36	42.83	44.09
$T^{\circ}\text{K}$	800	900	1000	1100	1200	1300
$-(F^0 - E_0^0)/T$	45.19	46.18	47.07	47.88	48.64	49.34
			47.07*	47.89*	48.66*	49.36*
$T^{\circ}\text{K}$	1400	1500	1600	1800	2000	2200
$-(F^0 - E_0^0)/T$	50.00	50.62	51.21	52.30	53.30	54.22
	50.03*	50.66*	51.26*	52.37*	53.38*	54.33*
$T^{\circ}\text{K}$	2400	2600	2800	3000		
$-(F^0 - E_0^0)/T$	55.08	55.88	56.64	57.35		
	55.20*	56.02*	56.80*	57.53*		

* The starred entries in Table I are computed from Mecke's fundamental frequencies, unstarred from those of Plyler.

in which $\bar{I} = 1.831 \times 10^{-40}$, $-R \ln 2$ is the Ehrenfest symmetry correction, and Q_v stands for the product of the state sums for three harmonic oscillators corresponding to the three fundamental modes of vibration of the molecule. The resulting values⁸ of $-(F^0 - E_0^0)/T$ are given in Table I. The nuclear spin contribution of the two hydrogen atoms ($2R \ln 2 = 2.754$) has not been included and must be added to the entries if they are to be used in conjunction with Giauque's table for hydrogen.⁹ The entropy follows at once from the relation $S^0 = -\partial F^0/\partial T$; for 298.1° (including the vibrational entropy 0.008, and the nuclear spin entropy 2.754) it is 47.93 cal./deg. In spite of the uncertainty as to the change in the spectroscopic constants in the higher rotational-vibrational states, the entries in Table I are probably accurate to two or three hundredth's of

a calorie per degree up to 1000°, with a considerably larger uncertainty at the highest temperatures.

Of the other gases involved in the water-gas reaction, the free energies of hydrogen⁹ and carbon monoxide¹⁰ are known, and an approximate calculation for carbon dioxide can be made from the data of Martin and Barker¹¹; they give $I = 70.8 \times 10^{-40}$, $\delta = 667.5$, $\nu(s) = 1286$, $\nu(a) = 2350 \text{ cm}^{-1}$, the deformation frequency δ being doubly degenerate. There is an additional complication due to the interaction of $\nu(s)$ with δ which tends to remove the degeneracy of some of the δ levels. The error introduced by neglecting this interaction, even at 1500°K, is not serious, and for lower temperatures is quite negligible. In computing the entries of Table II, this interaction was therefore ignored, but a rough idea of the

TABLE II. *The free energy of carbon dioxide.*

$T^{\circ}\text{K}$	298.1	300	400	500	600	700	800
$-(F^0 - E_0^0)/T$	43.575	43.62	45.85	47.69	49.28	50.68	51.94
$T^{\circ}\text{K}$	900	1000	1100	1200	1300	1400	1500
$-(F^0 - E_0^0)/T$	53.10	54.16	55.15	56.08	56.95	57.77	58.54

error introduced thereby can be obtained from considering the interaction of the levels $n_s = 2$, $n_s = 0$, $n_a = 0$ and $n_s = 0$, $n_s = 1$, $n_a = 0$. Ignoring the interaction, the contribution to the vibrational state sum is that of three coincident levels of energy $2 \times 667.5 = 1335 \text{ cm}^{-1}$ and a single level of energy 1286 cm^{-1} . In reality, there are four

distinct nondegenerate levels¹² of energy 1286, 1316, 1340 and 1388 cm^{-1} ; as far as the calculation of $-(F^0 - E_0^0)/T$ for 1500° is concerned, however, the use of the actual energy values for these two quantum states would only change the entry in Table II by 0.003 cal./deg. The values of $-(F^0 - E_0^0)/T$, computed in the usual way, are given in Table II for temperatures up to

⁸ In the calculations, the values of the universal constants are those given in *International Critical Tables*, Vol. I.

⁹ Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

¹⁰ Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

¹¹ Martin and Barker, Phys. Rev. **41**, 291 (1932).

¹² Badger and Sho-Chow Woo, J. Am. Chem. Soc. **54**, 3523 (1932).

1500°K, the corresponding entropy for 298.1° being 51.09. The numbers, even for the highest temperature of the table, are probably reliable to a few units in the second decimal place.

THE WATER-GAS EQUILIBRIUM

From Rossini's values for the heats of combustion of hydrogen¹³ and carbon monoxide¹⁴ (68,313 and 67,623 cal., respectively) and Osborne, Stimson and Fiock's value¹⁵ for the latent heat of vaporization of water (2439 joules per gram = 10,504 cal. per mole at 25°C), ΔH_{298} for the reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ is -9814 cal. Since the entropies of hydrogen⁹ and carbon monoxide¹⁰ are 33.98 and 47.31 for 298.1°, $\Delta S_{298.1}^\circ = -10.17$, and therefore $\Delta F_{298.1}^\circ$ is -6782 cal. From Tables I and II and the values of $-(F^\circ - E_0^\circ)/T$ at 298.1° for carbon monoxide and hydrogen, $\Delta E_0^\circ = -9636$ cal. The resulting $R \ln K = R \ln p_{\text{CO}} \cdot p_{\text{H}_2\text{O}} / p_{\text{CO}_2} \cdot p_{\text{H}_2}$ for the range 600°-1500° are given in Table III; in arriving at these

ments at five temperatures) the mean deviation is +0.06.

Emmett and Schultz¹⁶ obtained values of the equilibrium constant for this reaction from their data on the reduction of cobalt oxide by carbon monoxide and by hydrogen. The values of $R \ln K$ from their measurements at 723°, 788° and 843° are -3.95, -2.90 and -2.14, respectively, as compared with -3.91, -2.90 and -2.18 from Table III.

Giauque and Ashley¹⁷ have shown that the spectroscopic data lead to a value for the free energy of formation of steam in agreement with the best measurements on the mercuric oxide equilibria, and also in agreement with some calculations of their own for the Deacon reaction. It has been shown here that the same data lead to an equilibrium constant for the water-gas reaction which agrees with the most careful measurements of that quantity within the limits of error of the experiments.

TABLE III. The equilibrium constant for the water-gas reaction.

$K = p_{\text{CO}} \cdot p_{\text{H}_2\text{O}} / p_{\text{CO}_2} \cdot p_{\text{H}_2}$					
T°K	600	700	800	900	1000
-R ln K	6.49	4.32	2.74	1.54	0.62
T°K	1100	1200	1300	1400	1500
-R ln K	-0.11	-0.70	-1.18	-1.58	-1.91

values, entries in Table I based on Plyler's frequencies were used.

Neumann and Koehler³ found as the mean of a large number of measurements at 1259°, $K = 1.61$, i.e., $R \ln K = 0.947$; the value interpolated from Table II for this temperature is 1.00, i.e., $K = 1.65$. With four exceptions, their results for 700° to 1259° give $R \ln K$ which lie within ± 0.12 cal./deg. of the numbers obtained from Table III. For the range 1100°-1259° (measurements at seven different temperatures) the mean deviation of the experimental $R \ln K$ from the calculated is -0.05; for the range 900°-1100° (measurements at eight temperatures) the mean deviation is -0.04; and for the range 700°-900° (measure-

THE THERMAL DISSOCIATION OF STEAM

From Johnston and Walker's value¹⁸ for the entropy of oxygen at 298.1°, viz., 49.02, $\Delta S_{298.1}^\circ$ for the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(g)$ is -10.56; combining this with Rossini's value¹³ for $\Delta H_{298.1}$ (-57,809 cal.), $\Delta F_{298.1}^\circ = -54,661$; therefore, from the known free energies of hydrogen⁹ and oxygen,¹⁸ $\Delta E_0^\circ = -57,121$. The resulting $R \ln K = R \ln (p_{\text{H}_2\text{O}}) / (p_{\text{H}_2}) \cdot (p_{\text{O}_2})^{1/2}$ are given in Table IV for temperatures¹⁹ from 1300° to 3000°. As in the

TABLE IV. The equilibrium constant for the "oxygen" dissociation of steam.

$K = (p_{\text{H}_2\text{O}}) / (p_{\text{H}_2}) \cdot (p_{\text{O}_2})^{1/2}$						
T°K	1300	1400	1500	1600	1800	2000
R ln K	32.33	29.05	26.18	23.67	19.48	16.12
T°K	2200	2400	2600	2800	3000	
R ln K	13.36	11.05	9.07	7.38	5.90	

¹⁶ Emmett and Schultz, J. Am. Chem. Soc. **52**, 1782 (1930).

¹⁷ Giauque and Ashley, Phys. Rev. **43**, 81 (1933). Their value of ΔF for steam is -54,669, while the value obtained here is -54,661. The slight discrepancy arises from the fact that they used 10,490 as the latent heat of vaporization and 47.92 as the entropy.

¹⁸ Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

¹⁹ The oxygen numbers are subject to some uncertainty at the higher temperatures owing to the possible existence

¹³ Rossini, Bur. Standards J. Research **6**, 1 (1931).

¹⁴ Rossini, Bur. Standards J. Research **6**, 37 (1931).

¹⁵ Osborne, Stimson and Fiock, Bur. Standards J. Research **5**, 411 (1930).

case of the water-gas reaction, the numbers in Table I used in computing Table IV were those based on Plyler's frequencies.

A comparison of Table IV with the experimental data for the dissociation of steam is subject to some uncertainty. If the experimental results be accepted at their face value, the agreement between the $R \ln K$ obtained by various workers²⁰ for the temperature range 1300°–2200°K and the numbers obtained from Table IV is surprisingly close—in general within ± 0.3 cal./deg. Such agreement must be to some extent fortuitous, however, since Bonhoeffer and Reichardt²¹ have shown, qualitatively at any rate, that the “hydroxyl” equilibrium $\text{H}_2\text{O}=\text{OH}+\frac{1}{2}\text{H}_2$ is at least as important as the “oxygen” equilibrium computed in Table IV. Unfortunately a reliable calculation of the hydroxyl dissociation is not possible at present owing to the uncertainty as to the value of ΔE_0^0 for the reaction; until this point is settled, a comparison of the experimental results with Table IV is largely guess-work.

THE PRODUCER-GAS EQUILIBRIUM

From Rossini's¹⁴ heat of combustion of carbon monoxide (67,623 cal.) and Roth and Naeser's

a $^1\Delta$ level; see Lewis and von Elbe (J. Am. Chem. Soc. **55**, 511 (1933)). Such a level makes a contribution to $-(F^0-E_0^0)/T$ of approximately $2R/3 \exp[-17,200/RT]$, i.e., Johnston and Walker's values of $-(F^0-E_0^0)/T$ will be increased by 0.004 at 1500°K and by 0.074 at 3000°K; the corresponding $R \ln K$ will be decreased by one-half these amounts.

²⁰ Int. Crit. Tab., Vol. VII, p. 231.

²¹ Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928). Bonhoeffer and Reichardt's calculation of $K_{\text{OH}}=(p_{\text{H}_2\text{O}})/(p_{\text{H}_2})^{1/2} \cdot (p_{\text{OH}})$ is in error, since they did not allow correctly for the multiplicity of the rotational levels of the hydroxyl molecule. By using the spectroscopic constants given by Weizel (*Bandenspektren*, Leipzig, p. 327 (1931)) the values of $-(F^0-E_0^0)/T$ for hydroxyl are 48.35, 50.44, 52.11 and 53.50 for 1500°, 2000°, 2500° and 3000° respectively. The calculation is similar to that for NO discussed by Gordon and Barnes (J. Chem. Phys. **1**, 297 (1933)) except that the Π -doublet is inverted, with the result that the lowest observable state has $v=0$, $J=3/2$ for $^2\Pi_{1/2}$; the numbers just given include the item $R \ln 2$ which allows for the Δ -type doubling of the rotational levels but do not include the spin contribution of the hydrogen atom. If Bonhoeffer and Reichardt's estimate $\Delta E_0^0=-64$ Cal. for the reaction $\frac{1}{2}\text{H}_2+\text{OH}=\text{H}_2\text{O}$ be accepted, then $R \ln K_{\text{OH}}$ for the four temperatures is 27.2,

TABLE V. The equilibrium constant for the producer-gas reaction.

$$K = (p_{\text{CO}})^2/(p_{\text{CO}_2}).$$

$T^\circ\text{K}$	600	700	800	900	1000
$R \ln K$	-25.91	-16.10	-8.77	-3.10	+1.42
$T^\circ\text{K}$	1100	1200	1300	1400	1500
$R \ln K$	+5.09	+8.14	+10.69	+12.87	+14.75

heat of combustion of graphite²² as corrected by Clayton and Giauque,¹⁰ viz., 94,240 cal., $\Delta H_{298.1} = 41,006$ cal. for the reaction $\text{C}(\beta \text{ graphite}) + \text{CO}_2 = 2\text{CO}$. If the “third law” entropy of graphite (1.39 at 298.1°) be accepted, then $\Delta S_{298.1}^0 = 42.15$ and $\Delta F_{298.1}^0$ is 28,441 (corresponding to a free energy of formation for CO_2 at this temperature of -94,443 cal.) From Clayton and Giauque's tables for carbon monoxide and graphite, and Table II, $\Delta E_0^0 = 39,352$ cal.; the resulting $R \ln K = R \ln (p_{\text{CO}})^2/(p_{\text{CO}_2})$ are given in Table V for temperatures from 600° to 1500°K.

The experimental $R \ln K$ for the temperature range 1073°–1473°, obtained from the measurements of Rhead and Wheeler,²³ of Jellinek and Diethelm,²⁴ of Dent and Cobb²⁵ and of Becker²⁶ are quite self-consistent but are uniformly about 0.5 cal./deg. less than the corresponding numbers obtained from Table V. Of the quantities used in computing the table, there is no reason to suspect the heats of combustion or the spectroscopic entropies and free energies of the oxides of carbon. The position is different with respect to the graphite numbers, since it is possible that there is a “zero-point” entropy not included in the extrapolated integration to absolute zero. If *ad hoc*, for the sake of argument, a zero point entropy of 0.5 cal./deg. be assumed for graphite, the entropy at 298.1° will be 1.89, and all the entries in Clayton and Giauque's table of $-(F^0-E_0^0)/T$ will be increased by 0.5. $\Delta F_{298.1}^0$ for the producer-gas reaction will then be 28,590

16.0, 9.3 and 4.8 respectively. Since ΔE_0^0 is possibly in error by several kilo-calories, these $R \ln K_{\text{OH}}$ are uncertain to the extent of several calories per degree.

²² Roth and Naeser, Zeits. f. Elektrochemie **31**, 461 (1925).

²³ Rhead and Wheeler, J. Chem. Soc. **99**, 1140 (1911).

²⁴ Jellinek and Diethelm, Zeits. f. anorg. Chemie **124**, 203 (1922).

²⁵ Dent and Cobb, J. Chem. Soc. **1929**, p. 1903.

²⁶ Becker, J. Iron Steel Inst. (London) **121**, 337 (1930).

cal., all the $R \ln K$ in Table V will be decreased by 0.5 cal./deg., and the free energies of formation of the two oxides will be $-32,850$ cal. and $-94,290$ cal. for CO and CO₂, respectively. In a recent survey of this and other technical gas reactions, Chipman²⁷ gives 28,570 as the "best" experimental value of $\Delta F_{298.1}^0$ for the producer-gas reaction; the result obtained by assuming a zero point entropy for graphite of 0.5 cal./deg. is in very close agreement with his value.

A natural way to settle the question as to the

²⁷ Chipman, Ind. Eng. Chem. **24**, 1013 (1932).

proper value of the entropy of graphite would be to compute it from the entropy of carbon vapor, the vapor pressure of graphite, and the heat of sublimation. Unfortunately, the requisite experimental data²⁸ are not known with sufficient accuracy to permit such a calculation. The results for the producer-gas reaction suggest, however, that in other reactions involving graphite the possibility that the "third law" entropy is too small should be borne in mind.

²⁸ See a recent paper by Vaughan and Kistiakowsky, Phys. Rev. **40**, 457 (1932).