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The Free Energy of Sulphur Dioxide

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Values of $(F^\circ - E^\circ)/T$ for sulphur dioxide are computed from spectroscopic data; the heat of formation of sulphur dioxide from diatomic sulphur and oxygen is calculated from the calorimetric heats of formation of sulphur dioxide and hydrogen sulphide, and Cross' value for the energy of dissociation of hydrogen sulphide. Equilibrium constants for the reactions



are tabulated for the range 298.1 to 2800°K.

OF all the simpler gases the one which presented the greatest experimental difficulties in the determination of its free energy was probably sulphur dioxide. There was no appreciable dissociation at any attainable temperature, and the only values of its free energy of formation have been determined indirectly from other equilibria.^{1, 2, 3} The success that has attended the use of spectroscopic data in predicting equilibrium constants for other reactions suggests that the same method might be used for sulphur dioxide, although in this case the data are not as complete as one could wish.

For SO_2 the constants⁴ are: A , B , $C = 12.3$, 73.2 , 85.5×10^{-40} ; $\nu(\sigma) = 1378 - 8\nu_a$, $\nu(\pi) = 1150$, $\delta = 520 \text{ cm}^{-1}$. Ionescu gives no details of his rotational analysis, but his moments of inertia are consistent with Kohlrausch's value⁵ of the valence angle ($119^\circ 40'$) and with Wierl's value⁶ for the S-O distance (1.37A). The resulting $(F^\circ - E^\circ)/T$ are given in the second column of Table I. Since $(F^\circ - E^\circ)/T$ is known for sulphur vapor⁷ and for oxygen,⁸ the only additional information that is needed for a calculation of equilibria involving SO_2 is the value of ΔE°_0 or of ΔH_{298} for the reaction $\frac{1}{2}\text{S}_2(\text{g}) + \text{O}_2 = \text{SO}_2$.

TABLE I. $K_1 = (P_{\text{SO}_2})/(P_{\text{S}_2})^{1/2}(P_{\text{O}_2})$;
 $K_2 = (P_{\text{SO}})/(P_{\text{SO}_2})(P_{\text{O}_2})^{1/2}$.

| T°K | $-(F^\circ - E^\circ)/T$ | log K_1 | log K_2 | T°K | $-(F^\circ - E^\circ)/T$ | log K_1 | log K_2 |
|-------|--------------------------|-----------|-----------|------|--------------------------|-----------|-----------|
| 298.1 | 50.56 | 59.65 | 54.53 | 900 | 60.89 | 17.17 | 15.28 |
| 300 | 50.62 | 59.25 | 54.16 | 1000 | 62.01 | 15.06 | 13.34 |
| 350 | 51.93 | 50.24 | 45.84 | 1200 | 64.00 | 11.91 | 10.42 |
| 400 | 53.10 | 43.48 | 39.60 | 1400 | 65.73 | 9.65 | 8.33 |
| 500 | 55.11 | 34.02 | 30.85 | 1600 | 67.27 | 7.96 | 6.77 |
| 600 | 56.83 | 27.70 | 25.01 | 2000 | 69.92 | 5.60 | 4.59 |
| 700 | 58.33 | 23.19 | 20.84 | 2400 | 72.15 | 4.02 | 3.13 |
| 800 | 59.67 | 19.80 | 17.72 | 2800 | 74.06 | 2.90 | 2.09 |

Eckman and Rossini⁹ have measured the heat of combustion of rhombic sulphur ($\Delta H_{298} = -70,940 \pm 50 \text{ cal.}$) but thermal data for the reaction $\text{S}(\text{rh}) = \frac{1}{2}\text{S}_2(\text{g})$ are unknown. These can be obtained, however, with sufficient accuracy for the purpose in hand from the recent calculation of Cross¹⁰ for the hydrogen sulphide dissociation based on his rotational analysis of the hydrogen sulphide spectrum,¹¹ and the determination by Zeumer and Roth¹² of the heat of formation of hydrogen sulphide from rhombic sulphur and hydrogen ($\Delta H_{298} = -4800 \pm 150 \text{ cal.}$). Cross finds for the reaction $\text{H}_2 + \frac{1}{2}\text{S}_2(\text{g}) = \text{H}_2\text{S}$, $\Delta E^\circ_0 = -19,620 \text{ cal.}$; from this, and the spectroscopic free energies of hydrogen sulphide,¹⁰ sulphur¹³ and hydrogen,¹⁴ $\Delta F^\circ_{298.1} = -17,570 \text{ cal.}$ and since $S^\circ_{298.1}$ for H_2S , S_2 and H_2 is 49.15, 54.42 and 31.23, respectively, ΔH_{298} is $-20,340 \text{ cal.}$ Com-

¹ Lewis and Randall, *J. Am. Chem. Soc.* **40**, 362 (1918).

² Randall and Bichowsky, *J. Am. Chem. Soc.* **40**, 368 (1918).

³ Ferguson, *J. Am. Chem. Soc.* **40**, 1626, 1900 (1918).

⁴ Ionescu, *Comptes rendus* **196**, 1476 (1933); Smyth, *Phys. Rev.* **44**, 690 (1933). The universal constants used in the calculations of this paper are: $h = 6.554 \times 10^{-27}$, $k = 1.372 \times 10^{-16}$, $c = 2.9986 \times 10^{10}$, $R = 1.9869$, additive constant for the translational free energy = -7.267 .

⁵ Kohlrausch, *Physik. Zeits.* **33**, 165 (1932).

⁶ Wierl, *Ann. d. Physik* **8**, 521 (1931).

⁷ Montgomery and Kassel, *J. Chem. Phys.* **2**, 417 (1934).

⁸ Johnston and Walker, *J. Am. Chem. Soc.* **55**, 172 (1933).

⁹ Eckman and Rossini, *Bur. Standards J. Research* **3**, 597 (1929).

¹⁰ Cross, *J. Chem. Phys.* **3**, 168 (1935).

¹¹ Cross, *Phys. Rev.* **46**, 536 (1934); **47**, 7 (1935).

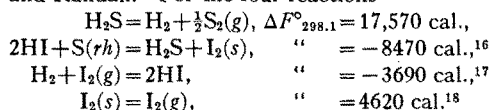
¹² Zeumer and Roth, *Zeits. f. Elektrochemie* **40**, 777 (1934).

¹³ In the calculations of this paper, Montgomery and Kassel's values of $-(F^\circ - E^\circ)/T$ (reference 7) have been increased by 0.55 cal./degree as recommended by Cross (reference 10).

¹⁴ Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930).

binning this value with Zeumer and Roth's result, it follows that ΔH_{298} for the reaction $S(rh) = \frac{1}{2}S_2(g)$ is 15,540 cal., and consequently ΔH_{298} for the reaction $\frac{1}{2}S_2(g) + O_2 = SO_2$ is -86,480 cal. Since $S^\circ_{298.1}$ for oxygen⁸ and for sulphur dioxide is 49.02 and 59.02, respectively, $\Delta F^\circ_{298.1}$ for the formation of SO_2 from diatomic sulphur and oxygen is -81,350 cal. and ΔE°_0 is -85,860 cal.

There is an alternative method of obtaining the heat of vaporization of diatomic from rhombic sulphur similar to that used by Lewis and Randall.¹⁵ For the four reactions



Hence for the reaction $S(rh) = \frac{1}{2}S_2(g)$, $\Delta F^\circ_{298.1} = 10,030$ cal., and, since the third law entropy of rhombic sulphur is 7.69 cal./degree,¹⁹ ΔH_{298} for this reaction is 15,850 cal., which agrees with the previous result (15,540 cal.) probably as closely as can be expected.

In the third column of Table I are given the values²⁰ of $\log K_1 = \log (P_{SO_2})/(P_{S_2})^{1/2}(P_{O_2})$, computed from the spectroscopic values of $(F^\circ - E^\circ_0)/T$ for the constituents, on the assumption that ΔE°_0 for the reaction is -85,860 cal. In the last column are the equilibrium constants for the "sulphur monoxide" dissociation of SO_2 , $\log K_2 = \log (P_{SO_2})/(P_{SO})(P_{O_2})^{1/2}$; these were obtained by means of Montgomery and Kassel's table of $(F^\circ - E^\circ_0)/T$ for SO , on the assumption that ΔE°_0 for the reaction $SO + \frac{1}{2}O_2 = SO_2$ is -79,300 cal. It is evident that the equilibrium constant for the reaction $\frac{1}{2}S_2(g) + SO_2 = 2SO$, is given by the relation $\log (P_{SO})^2/(P_{S_2})^{1/2}(P_{SO_2}) = \log K_1 - 2 \log K_2$.

Of the equilibria involving SO_2 which have been studied experimentally, Randall and Bichowsky's measurements² for the reaction $SO_2 + 3H_2 = 2H_2O + H_2S$ and Ferguson's³ for the re-

action $SO_2 + 2CO = \frac{1}{2}S_2(g) + 2CO_2$ can be compared with the results of calculation. For the former, from Rossini's value²¹ for the heat of formation of steam, ΔE°_0 for the reaction is -47,980 cal.; from this and the known free energies of hydrogen,¹⁴ steam²² and hydrogen sulphide,¹⁰ $\log (P_{H_2O})^2(P_{H_2S})/(P_{SO_2})(P_{H_2})^3$ for 1160°, 1362°, 1473° and 1645°K is 5.58, 4.06, 3.40 and 2.54, respectively. Randall and Bichowsky found for the same four temperatures 5.93, 4.32, 3.54 and 2.56. Calculation shows that the amount of sulphur monoxide present under the conditions of their experiments is quite negligible, and also (from the data of Montgomery and Kassel) that the dissociation of diatomic into monatomic sulphur can likewise be ignored. There is thus a discrepancy of about 1.6 cal./degree in $R \ln K$ at the lowest of their temperatures, this difference decreasing rapidly as the temperature rises. This improvement in the agreement is perhaps significant, since one would expect *caeteris paribus* that equilibrium would be the more readily established the higher the temperature. It should be noted in passing that the revised free energy equation of Eastman²³ for SO_2 combined with the spectroscopic free energies of formation of H_2O and H_2S gives for $\log K$ at the same four temperatures, 6.50, 4.97, 4.30 and 3.43—definitely in worse agreement with Randall and Bichowsky's results than are those obtained above.

For the second reaction, studied by Ferguson, from Rossini's heat of combustion of carbon monoxide²⁴ and the spectroscopic free energies,²⁵ $\log (P_{SO_2})(P_{CO})^2/(P_{S_2})^{1/2}(P_{CO_2})^2$ for 1275° and 1460°K is -3.07 and -2.02, respectively; Ferguson found -3.56 and -2.38. The disagreement between the results of calculation and experiment is thus definitely greater than the apparent uncertainty in the experimental data (± 0.2 in $\log K$) on the one hand and in the calculated thermodynamic quantities on the other, although here again the discrepancy decreases with rise in temperature.

¹⁵ Lewis and Randall, *Thermodynamics*, 1923, p. 540 *et seq.*

¹⁶ Pollitzer, *Zeits. f. anorg. Chemie* **64**, 121 (1909).

¹⁷ Zeise, *Zeits. f. Elektrochemie* **40**, 885 (1934).

¹⁸ Baxter, Hickey and Holmes, *J. Am. Chem. Soc.* **29**, 127 (1907); Giauque, *J. Am. Chem. Soc.* **53**, 507 (1931).

¹⁹ *Int. Crit. Tab.* **5**, 89.

²⁰ A preliminary table of $\log K_1$ is given in a recent review article by Zeise, *Zeits. f. Elektrochemie* **40**, 885 (1934). The values given there differ slightly from those of this paper, since at that time Cross' calculations for hydrogen sulphide had not appeared.

²¹ Rossini, *Bur. Standards J. Research* **6**, 1 (1931).

²² Gordon, *J. Chem. Phys.* **2**, 65, 549 (1934).

²³ Eastman, *Bur. Mines Infor. Circ. No. 6454* (1931).

²⁴ Rossini, *Bur. Standards J. Research* **6**, 37 (1931).

²⁵ For CO , Clayton and Giauque, *J. Am. Chem. Soc.* **55**, 5071 (1933); for CO_2 , Kassel, *J. Am. Chem. Soc.* **56**, 1838 (1934).