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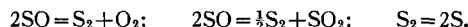


# The Free Energy of Sulfur Monoxide and the Dissociation Constants of S<sub>2</sub><sup>1</sup>

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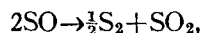
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Values of  $(F^0 - E_0^0)/T$  are calculated from spectroscopic data for S<sub>2</sub>, SO and S, and equilibrium constants obtained for the reactions



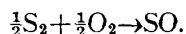
It is found that SO is stable with respect to the first mode of decomposition, but unstable with respect to the second except at higher temperatures.

VICTOR HENRI<sup>4</sup> originally postulated SO to explain a band system lying between 2500Å and 3900Å observed by him in the emission spectrum from a discharge tube containing sulfur dioxide. Recently, Schenk and others<sup>5</sup> have succeeded in isolating pure SO from the product formed in a condensed electric discharge through sulfur dioxide or a mixture of sulfur vapor and sulfur dioxide at low pressures. They find that at 100°C or at pressures exceeding 50 mm a rapid decomposition sets in according to the equation



but that at room temperature and lower pressures the gas is quite stable and may be kept for some days in dry vessels. At room temperature there is no reaction with oxygen. The existence of SO as an intermediate compound is indicated spectroscopically for a number of reactions.

In view of the stability of SO it has seemed worth while to calculate from spectroscopic data the free energy change and equilibrium constants for the formation from gaseous S<sub>2</sub> and O<sub>2</sub>,



The  $F^0/T$  values for S<sub>2</sub> have also been used to calculate equilibrium constants for



The mathematical methods employed are those given by Kassel.<sup>6</sup> Values of  $(F^0 - E_0^0)/T$  for O<sub>2</sub> have already been calculated by Johnston and Walker.<sup>7</sup> No correction has been made for the low-lying <sup>1</sup>Δ state,<sup>8,9</sup> the effect of which is certainly negligible at all but the highest one or two temperatures calculated. From the recent analyses of Martin<sup>10</sup> and Naudé and Christy<sup>11</sup> the necessary spectroscopic constants for both SO and S<sub>2</sub> are accurately known. Making minor algebraic rearrangements we may write from Martin's work for the energy levels of SO

$$\begin{aligned} \epsilon = & 0.70613(1 - 0.00796171v)j(j+1) \\ & - (1.12884 \times 10^{-6} - 3.20 \times 10^{-10}v)(j + \frac{1}{2})^4 \\ & + 1117.61v - 6.116v^2 \end{aligned}$$

and, from the results of Naudé and Christy for S<sub>2</sub>

$$\begin{aligned} \epsilon = & 0.40865(1 - 0.00171296v)j(j+1) \\ & - 5.2 \times 10^{-7}(j + \frac{1}{2})^4 + 724.5v - 2.91v^2. \end{aligned}$$

Both molecules have <sup>3</sup>Σ normal states. A small unavoidable error is introduced through ignorance of the triplet separations and failure to treat the component levels separately. In the case of S<sub>2</sub> account must be taken of the missing alternate rotational levels. Dissociation from the lower states of SO and S<sub>2</sub> gives normal atoms, the energies of dissociation being for SO,  $D'' = 5.053v$ , and for S<sub>2</sub>,  $D'' = 4.45v$ . These values, together with  $D''$  for O<sub>2</sub><sup>7</sup> give  $\Delta E_0^0 = -6561$  cal. The atomic energy levels used in the

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<sup>4</sup> Henri and Wolff, J. Phys. et Rad. **10**, 81 (1929).

<sup>5</sup> (a) Schenk, Zeits. f. anorg. Chemie **211**, 150 (1933).

(b) Cordes and Schenk, Trans. Farad. Soc. **30**, 31 (1934).

<sup>6</sup> Kassel, J. Chem. Phys. **1**, 576 (1933).

<sup>7</sup> Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

<sup>8</sup> Mulliken, Phys. Rev. **32**, 186 (1928).

<sup>9</sup> Lewis and von Elbe, Phys. Rev. **41**, 678 (1932).

<sup>10</sup> Martin, Phys. Rev. **41**, 167 (1932).

<sup>11</sup> (a) Naudé and Christy, Phys. Rev. **37**, 490 (1931). (b) Christy and Naudé, Phys. Rev. **37**, 903 (1931).

calculation of  $(F^0 - E_0^0)/T$  for S are taken from Bacher and Goudsmit.<sup>12</sup> The lowest lying levels belong to an inverted  $^3P$  state with separations of 398 and 174  $\text{cm}^{-1}$ . These are the only levels sufficiently low to have any appreciable effect, the next lowest level, a  $^5S_2^0$ , being more than 52,000  $\text{cm}^{-1}$  higher.

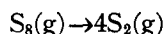
The results of the calculations from spectroscopic data are shown in Table I. The anharmonic

TABLE I. Free energies and equilibrium constants for SO,  $\text{O}_2$ ,  $\text{S}_2$  and S.

$T(^{\circ}\text{K})$	$-\left(\frac{F^0 - E_0^0}{T}\right)_{\text{S}_2}$	$-\left(\frac{F^0 - E_0^0}{T}\right)_{\text{SO}}$	$-\left(\frac{F^0 - E_0^0}{T}\right)_{\text{S}}$	$K = \frac{(\text{SO})}{(\text{S}_2)^{1/2}(\text{O}_2)^{1/2}}$	$\log_{10} K = \frac{(\text{SO})}{(\text{S}_2)^{1/2}(\text{O}_2)^{1/2}}$
250	45.435	44.838	33.824	5.179	-84.896
298.1	46.690	46.068	34.757	5.179	-70.280
300	46.736	46.112	34.791	5.148	-69.799
350	47.850	47.196	35.618	4.463	-58.996
400	48.829	48.141	36.338	3.949	-50.882
450	49.703	48.982	36.976	3.549	-44.562
500	50.495	49.740	37.547	3.228	-39.499
550	51.219	50.433	38.064	2.966	-35.352
600	51.887	51.070	38.535	2.748	-31.892
700	53.085	52.215	39.369	2.405	-26.447
800	54.138	53.221	40.089	2.147	-22.356
900	55.079	54.121	40.721	1.947	-19.169
1000	55.929	54.937	41.284	1.787	-16.615
1250	57.757	56.694	42.470	1.500	-12.008
1500	59.273	58.160	43.431	1.308	-8.928
1750	60.571	59.418	44.239	1.172	-6.722
2000	61.705	60.522	44.934	1.069	-5.063
2500	63.620	62.393	46.089	0.926	-2.733
3000	65.200	63.943	47.027	0.831	-1.172
4000	67.722	66.427	48.498	0.711	+ 0.789
5000	69.701	68.382	49.632	0.639	+ 1.974

corrections for SO and  $\text{S}_2$  were calculated directly for 250, 298.1, 500, 1000, 2000, 3000, 4000 and 5000°K and carefully interpolated for the other values. The values of column 4 were calculated directly for all the temperatures except 350, 450 and 550°K.

In Table II are given a few values for the equilibrium pressure of SO in contact with liquid or solid sulfur and  $\text{O}_2$  (1 atm.). These values are calculated from Table I, vapor pressures of sulfur given by Gruener,<sup>13</sup> and equilibrium constants for the reaction



extrapolated from the results of Preuner and Schupp.<sup>14</sup> As the thermal data are uncertain, these figures must be interpreted as giving only the order of magnitude of the SO pressure. The accuracy is sufficient, however, to demonstrate the stability of SO with respect to  $\text{S}_2$  and  $\text{O}_2$ .

<sup>12</sup> Bacher and Goudsmit, *Atomic Energy States*, p. 397. McGraw-Hill Co. (1932).

<sup>13</sup> Gruener, *Zeits. f. anorg. Chemie* **56**, 149 (1908).

<sup>14</sup> Preuner and Schupp, *Zeits. f. physik. Chemie* **68**, 129 (1909).

TABLE II. Equilibrium pressures of SO.

$T(^{\circ}\text{K})$	Form of sulfur present	Equilibrium pressure of SO (mm)	
		1 atm. $\text{O}_2$	1 atm. $\text{SO}_2$
298.1	rhombic	17.8	$2.94 \times 10^{-25}$
350	rhombic	123	$1.59 \times 10^{-20}$
400	monoclinic	540	$4.10 \times 10^{-17}$
450	liquid	1560	$1.79 \times 10^{-14}$
700	1 atm. $\text{S}_2$	—	$1.54 \times 10^{-6}$
1000	1 atm. $\text{S}_2$	—	$4.05 \times 10^{-3}$
1500	1 atm. $\text{S}_2$	—	1.82
2000	1 atm. $\text{S}_2$	—	37.8

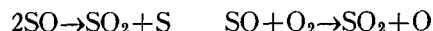
$\Delta F^0$  for the reaction



is directly calculable from Table I and the revised free energy equation for  $\text{SO}_2$  given by Eastman.<sup>15</sup> Table II gives also the pressure of SO in equilibrium with  $\text{SO}_2$  (1 atm.) at several temperatures above and below the boiling point of sulfur. The values at the four highest temperatures are calculated for  $\text{S}_2$  (1 atm.), the others for solid or liquid sulfur. The results indicate that SO is moderately stable with respect to  $\text{S}_2$  and  $\text{SO}_2$  at flame temperatures, but very unstable below 1000°K.

The dissociation constants for  $\text{S}_2$  are given in Table I. These results show that the inconsistent experimental data of Nernst<sup>16</sup> are subject to large errors. This same conclusion is supported by other experimental investigations.<sup>17</sup>

The heat of dissociation of  $\text{SO}_2$  to SO and S(g) is about 135,000 cal. and hence the reactions



are 15–20,000 cal. exothermic. It is quite likely, however, that both reactions have activation energies of the order of 50,000 cal. The decomposition of SO is therefore probably a chain reaction, with a lower pressure limit of some 50 mm, and it may be predicted that the oxidation will also be a chain reaction. We may conclude that SO is a respectable substance; it is no more a free radical than  $\text{O}_2$ , and it is only slightly more susceptible to chain decomposition than are ozone and acetylene.

<sup>15</sup> Eastman, Bureau of Mines Information Circular 6454 (1931).

<sup>16</sup> Nernst, *Zeits. f. Elektrochemie* **9**, 622 (1903).

<sup>17</sup> See for example, V. Meyer and Biltz, *Zeits. f. physik. Chemie* **4**, 266 (1889).