

Thermodynamic Properties of Sulfur Compounds II. Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

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Thermodynamic Properties of Sulfur Compounds

II. Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide

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(Received October 7, 1935)

The thermodynamic properties of sulfur dioxide, carbon disulfide, and carbonyl sulfide are calculated from the molecular constants obtained by electron diffraction and Raman and infrared spectra. $-(F^0 - E_0^0)/T_{298.1} = 50.95, 48.28, 47.39$; $S^0_{298.1} = 59.40, 56.84, 55.34$ for SO_2 , $\text{CS}_2(\text{g})$, and COS , respectively. The results are applied to several reactions involving these compounds. The free energies of formation of $\text{CS}_2(\text{l})$ and COS at 298.1°K are $+15.24$ and -40.48 kg.cal.

THE results of the preceding paper¹ give the following values for terms which appear in the approximate equations for the entropy and free energy functions such as given by Kassel:²

$$\begin{aligned}\text{SO}_2, \quad \frac{1}{2}R \ln I_A I_B I_C &= -262.93, R \ln \mu = -1.377, \\ \text{CS}_2, \quad R \ln I &= -172.03, R \ln \mu = -1.377, \\ \text{COS}, \quad R \ln I &= -173.23, R \ln \mu = 0.\end{aligned}$$

The vibration frequencies were taken as follows:

$$\begin{aligned}\text{SO}_2, \quad 1361, 1152, 525,^3 \\ \text{CS}_2, \quad 1523, 655.5, 396.8 (2),^4 \\ \text{COS}, \quad 2079, 859, 527 (2).^5\end{aligned}$$

Because of the lack of adequate data to determine the anharmonic factors, the molecules were treated as harmonic oscillators and the vibrational contributions determined from the tables of Gordon and Barnes.⁶ This also ignores the Fermi interaction, but the errors introduced are not serious for work of the accuracy intended herein.

The results shown in Table I were obtained from the equations;

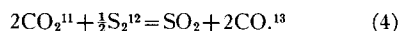
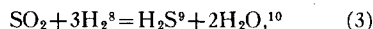
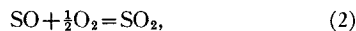
$$\begin{aligned}\text{SO}_2, \quad (F^0 - E_0^0)/T &= -4R \ln T - 5.49 \\ &\quad + [(F^0 - E_0^0)/T]_{\text{vib.}}, \\ S^0 &= 4R \ln T + 13.44 + S_{\text{vib.}},\end{aligned}$$

$$\begin{aligned}\text{CS}_2, \quad (F^0 - E_0^0)/T &= -(7/2)R \ln T - 7.93 \\ &\quad + [(F^0 - E_0^0)/T]_{\text{vib.}}, \\ S^0 &= (7/2)R \ln T + 14.88 + S_{\text{vib.}}, \\ C_p^0 &= 6.954 + C_{\text{vib.}}, \\ \text{COS}, \quad (F^0 - E_0^0)/T &= -(7/2)R \ln T - 7.40 \\ &\quad + [(F^0 - E_0^0)/T]_{\text{vib.}}, \\ S^0 &= (7/2)R \ln T + 14.35 + S_{\text{vib.}}, \\ C_p^0 &= 6.954 + C_{\text{vib.}}.\end{aligned}$$

The values for SO_2 are probably accurate to within 0.15 unit, while those for CS_2 and COS should be within 0.1 unit of the true values.

SULFUR DIOXIDE

A similar calculation for SO_2 has recently been made by Gordon,⁷ who applied his results to the reactions



(References are to the sources of $(F^0 - E_0^0)/T$ values.) Since the new values of $-(F^0 - E_0^0)/T$ are 0.38 larger than Gordon's, the values of $\log K_1$ and $\log K_2$ in Gordon's Table I should be in-

* National Research Fellow in Chemistry, 1933-35. Now at Stanford.

† No. 502.

¹ P. C. Cross and L. O. Brockway, *J. Chem. Phys.* **3**, 821 (1935).

² L. Kassel, *J. Am. Chem. Soc.* **55**, 1351 (1933).

³ R. M. Badger and L. G. Bonner, *Phys. Rev.* **43**, 305 (1933).

⁴ D. M. Dennison and N. Wright, *Phys. Rev.* **38**, 2077 (1931).

⁵ C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. A* **140**, 605 (1933).

⁶ A. R. Gordon and C. Barnes, *J. Chem. Phys.* **1**, 297 (1933).

⁷ A. R. Gordon, *J. Chem. Phys.* **3**, 336 (1935).

⁸ W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930).

⁹ P. C. Cross, *J. Chem. Phys.* **3**, 168 (1935).

¹⁰ A. R. Gordon, *J. Chem. Phys.* **1**, 308 (1933).

¹¹ L. Kassel, *J. Am. Chem. Soc.* **56**, 1838 (1934).

¹² C. W. Montgomery and L. Kassel, *J. Chem. Phys.* **2**, 417 (1934). Corrected by Cross, reference 9.

¹³ J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.* **55**, 5071 (1933).

TABLE I. Free energy, entropy, and heat capacity of SO_2 , CS_2 , and COS .

T	SO_2	$-(F^0 - E_0^0)/T$ ($CS_2(g)$)	COS	SO_2	S^0 ($CS_2(g)$)	COS	SO_2	C_p^0 ($CS_2(g)$)	COS
298.1	50.95	48.28	47.39	59.40	56.84	55.34	9.51	10.91	9.92
400	53.49	50.90	49.81	62.32	60.19	58.41	10.35	11.85	10.95
500	55.50	53.04	51.79	64.72	62.91	60.93	11.08	12.52	11.66
600	57.21	54.89	53.50	66.79	65.24	63.11	11.67	13.00	12.21
700	58.71	56.51	55.01	68.62	67.27	65.03	12.11	13.37	12.64
800	60.05	57.97	56.37	70.26	69.08	66.74	12.44	13.65	12.98
900	61.27	59.30	57.61	71.74	70.70	68.28	12.70	13.86	13.26
1000	62.39	60.51	58.75	73.09	72.16	69.69	12.90	14.02	13.49
1100	63.42	61.63	59.81	74.33	73.50	70.98	13.05	14.15	13.68
1200	64.37	62.67	60.79	75.47	74.74	72.18	13.17	14.26	13.84
1300	65.27	63.65	61.71	76.53	75.89	73.30	13.27	14.35	13.97
1400	66.11	64.57	62.58	77.52	76.96	74.34	13.35	14.42	14.08
1500	66.91	65.44	63.40	78.44	77.97	75.31	13.42	14.48	14.17
1600	67.66	66.25	64.17	79.30	78.91	76.22	13.47	14.53	14.25
1700	68.37	67.02	64.90	80.12	79.79	77.09	13.52	14.57	14.32
1800	69.04	67.75	65.60	80.90	80.61	77.91	13.56	14.61	14.38

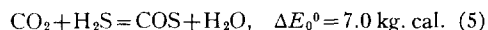
TABLE II.

Eq.	Reactions	ΔE_0^0	$\Delta F^0/T = -R \ln K$				
			$T = 298.1$	400	600	900	1500
(3)	$3H_2 + SO_2 = H_2S + 2H_2O$	-47.98	-152.2	-109.7	-67.5	-38.5	-14.5
(4)	$2CO_2 + \frac{1}{2}S_2 = 2CO + SO_2$	47.65	139.0	97.2	56.5	29.4	8.1
(5)	$CO_2 + H_2S = COS + H_2O$	7.0	23.7	17.6	11.5	7.4	4.3
(6)	$COS + H_2S = CS_2 + H_2O$	8.4	31.3	23.9	16.7	11.8	8.0
(17)	$CO + \frac{1}{2}S_2 = COS$	-22.2	-57.9	-38.3	-19.1	-6.4	-3.6
(18)	$2COS = CO_2 + CS_2$	1.4	7.6	6.4	5.2	4.4	3.8
(19)	$CS_2 = C(\text{graph}) + S_2$	3.6	12.6	9.7	6.9	5.2	3.8

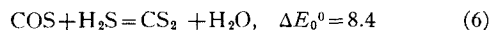
creased by 0.08. By using the values of ΔE_0^0 suggested by Gordon, several values of $\Delta F^0/T = -R \ln K$ have been calculated for reactions (3) and (4) and given in Table II. Comparisons with experimental results are found in Table III.

CARBON DISULFIDE AND CARBONYL SULFIDE

Since the thermal measurements on these compounds are known to be subject to some errors, values of ΔE_0^0 were obtained from equilibrium measurements. The results of Terres and Weseman¹⁴ on the reactions

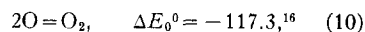
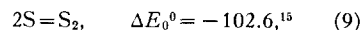
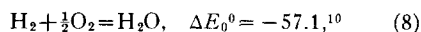


and



gave exceptionally consistent results having no pronounced trend with temperature.

From the reactions



one obtains

$$E_0^0(H_2O) - E_0^0(H_2S) = -44.9. \quad (11)$$

Combining with the results on reactions (5) and (6) gives

$$E_0^0(COS) - E_0^0(CO_2) = 51.9, \quad (12)$$

$$E_0^0(CS_2) - E_0^0(COS) = 53.3 \quad (13)$$

Since $E_0^0(CO) - E_0^0(CO_2) = 125.4,^{11} \quad (14)$

$$E_0^0(CO) - E_0^0(CS_2) = 20.2, \quad (15)$$

¹⁵ A. Christy and S. M. Naudé, Phys. Rev. **37**, 903 (1931).

¹⁶ B. Lewis and G. von Elbe, J. Am. Chem. Soc. **57**, 612 (1935).

¹⁴ E. Terres and H. Weseman, Zeits. f. angew. Chemie **45**, 795 (1932).

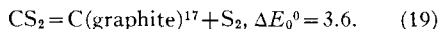
TABLE III.

Eq.	T	Calc.	$-R \ln K$ Obs.	Ref.	Calc.- Obs.
(3)	1160	-25.1	-27.1	18	+2.0
	1362	-18.2	-19.8	18	+1.6
	1473	-15.2	-16.2	18	+1.0
	1645	-11.2	-11.7	18	+0.5
(4)	1275	13.7	16.3	19	-2.6
	1460	8.9	10.9	19	-2.0
(5)	623	11.2	11.3	14	-0.1
	673	10.3	10.3	14	0
	723	9.5	9.5	14	0
	773	8.8	8.8	14	0
	823	8.2	8.2	14	0
	873	7.7	7.5	14	+0.2
(6)	973	11.1	11.3	14	-0.2
	1023	10.7	11.0	14	-0.3
	1073	10.3	10.3	14	0
	1123	9.9	9.7	14	+0.2
	1173	9.6	9.0	14	+0.6
(17)	533	23.9	22.5	20	+1.4
	575	20.7	19.1	20	+1.6
	1073	2.3	2.2	21	+0.1
	1223	-0.2	-1.4	21	+1.2
(18)	533	5.5	8.2	22	-2.7
	575	5.3	9.4	22	-4.1
	573	5.3	5.3	21	0
	673	4.9	4.9	21	0
	753	4.7	3.7	21	+1.0

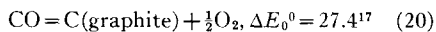
$$E_0^0(\text{CO}) - E_0^0(\text{COS}) = 73.5. \quad (16)$$

These results are expressed as differences inasmuch as there still seems to be some doubt as to the absolute values of E_0^0 for carbon compounds.

The E_0^0 differences given here have been applied to the reactions



The reaction

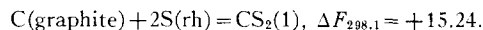
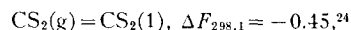


was also employed to obtain ΔE_0^0 for reaction (19). The results are summarized in Tables II and III.

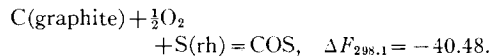
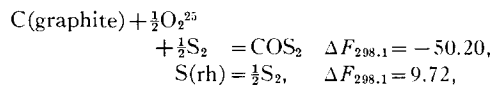
¹⁷ J. O. Clayton and W. F. Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

The comparisons on reactions (17) and (18) are satisfactory considering that the values of Lewis and Lacey on (18) are admittedly only approximate. The large discrepancies between observed and calculated results for (19) have been discussed by Randall.²³ The experimental measurements are in such poor agreement with each other that it seems justified to consider the indirectly calculated values as the most reliable so far available. The experimental results are not given here because this reaction will be considered more fully in a forthcoming paper by Professor Randall.

The free energies of formation of CS_2 and COS may be obtained from these results as follows:



The value obtained from a rather uncertain value of the heat of combustion of CS_2 is 17.15.²⁴



This value is in essential agreement with the thermal value of -39.80 .²⁴

¹⁸ M. Randall and F. R. Bichowsky, J. Am. Chem. Soc. **40**, 368 (1918).

¹⁹ J. B. Ferguson, J. Chem. Soc. **40**, 1626, 1900 (1918).

²⁰ Lewis and Randall, *Thermodynamics* (1923), p. 581. Recalculated with Gordon's value for the free energy of formation of S_2 , reference 7.

²¹ A. Stock, W. Siecke and E. Pohland, Ber. **57**, 719 (1924).

²² G. N. Lewis and W. N. Lacey, J. Am. Chem. Soc. **37**, 1976 (1915).

²³ Randall, Am. Chem. Soc. San Francisco, August, 1935.

²⁴ Parks and Huffman, *Free Energies of Some Organic Compounds* (1932), pp. 204-206.

²⁵ H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **55**, 172 (1933).