lene concentrations and short contact times used in these studies, together with an analytical method yielding virtually continuous analyses, have made it possible to observe the conditions which obtain during the *formation* of the reactive surface layer; whereas the usual experimental procedures observe only the steady state conditions.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermal Dissociation of Sulfur Dioxide and the Dissociation Energy of SO and S_2

BY GEORGE ST. PIERRE AND JOHN CHIPMAN

RECEIVED MARCH 10, 1954

The ratio j = $Fe^{+++}/(Fe^{+++} + Fe^{++})$ in lime–iron oxide slags in equilibrium with SO_2 or SO_2–CO mixtures is used to determine the partial pressure of O_2 in the gas at 1550°. The products of dissociation of SO_2 at this temperature are principally SO and O_2. The data lead to a decision between possible values for the dissociation energies of SO and S_2 in favor of 5.146 and 3.6 e.v., respectively. The free energy of formation of SO from S_2 and O_2 at 298.16 and 1823°K., respectively, is −18.6 and −20.6 kcal./mole.

Introduction

The dissociation products of sulfur dioxide at high temperatures include S_2, O_2, SO, SO_3, S and O. Equilibrium concentrations under given conditions are unknown because of major uncertainties in the heats of formation of S_2 and SO from the atoms. The importance of these gases in many pyrometallurgical processes, in particular their reactions with slags containing oxygen and sulfur, has led to this study. Data will be presented which establish the oxygen pressure at 1550° in pure SO_2 and in several SO_2–CO mixtures which lead to a clear choice among the proposed values for the uncertain heats of formation.

TABLE I

SUMMARY OF THERMODYNAMIC PROPERTIES AT 1823°K.

	S	O	S_2^a	O_2	SO^a	SO_2^a	CO	CO_2	COS^b	SO_3^a
$-(F° - E°_0)/T$	44.453	42.539	61.66	55.369	59.82	69.20	53.369	60.76	65.75	75.53
$(H° - E°_0)/T$	5.222	5.080	8.49	8.025	8.21	12.01	7.739	11.84	12.36	17.62
S^0	49.675	47.620	70.15	63.394	68.03	81.21	61.108	72.60	78.11	93.15

[a] Extrapolated from 1500°K. using C_p data. [b] Extrapolated from 1800°K. using C_p data.

Spectroscopic and Thermochemical Data.—Data on the thermodynamic properties of all the gases under consideration are presented in Table I. The data for each gas except COS have been taken from "Selected Values of Chemical Thermodynamic Properties."[1] The values for COS are those given by Cross.[2]

In Table II are summarized data on some heats of formation.

The several heats of formation of SO and S_2 from the atoms arising from different interpretations of the spectroscopic measurements are reported. According to Gaydon,[3] if the predissociation limit of 41,520 cm.$^{-1}$ for SO is due to a $^3\pi$ state arising from normal atoms, then the dissociation energy is 5.146 e.v.; however, if it goes to $O(^3P)$ and $S(^1D)$ then the dissociation energy is 4.002 e.v. Gaydon favored the first interpretation while Herzberg[4] chose the latter. The situation for S_2 is similarly uncertain and it appears that the two values for SO and the three values for S_2 are equally probable. Six different values for the heat of formation of SO from S_2 and O_2 are given in Table III.

TABLE II

SUMMARY OF DATA ON HEATS OF FORMATION

Reaction	$\Delta H°_0$ E.v./mole	$\Delta H°_0$ Kcal./mole	$\Delta H°_{298.16}$, kcal./mole	Method of determ.	Reference
S + O = SO	−4.002	− 92.3		Spect.	a,b,c
	−5.146	−118.7			
$2S = S_2$	−3.3	− 76			
	−3.6	− 83		Spect.	a,b,d,e,p
	−4.4	−101			
$2O = O_2$	−5.115	−117.96		Spect.	a,b,n
$^1/_2S_2 + O_2 = SO_2$		− 85.74	−86.36	Calor. Equil.	f,g,h,i j,k,l,o
$CO + {}^1/_2O_2 = CO_2$		− 66.767	−67.636	Calor.	f
$CO + {}^1/_2S_2 = COS$		− 21.01	−21.78	Calor. Equil.	f,m
$SO_2 + {}^1/_2O_2 = SO_3$		− 22.70	−23.47	Calor.	f

[a] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947. [b] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," 1st Ed., Prentice–Hall Inc., Co., New York, N. Y., 1939; 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950. [c] E. V. Martin, *Phys. Rev.*, **41**, 167 (1932). [d] E. Olsson, *Z. Physik*, **100**, 656 (1936). [e] G. M. Naude and A. Christy, *Phys. Rev.*, **37**, 490 (1931). [f] "Selected Values of Chem. Therm. Prop., Circ. 500," Natl. Bur. Std., 1952. [g] E. D. Eastman, *Bur. Mines Inform. Circ.*, **6454** (1931). [h] J. R. Eckman and F. D. Rossini, *J. Research Natl. Bur. Standards*, **3**, 597 (1929). [i] J. B. Ferguson, THIS JOURNAL, **40**, 1626 (1918); **41**, 69 (1919). [j] G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 157 (1909). [k] A. R. Gordon, *J. Chem. Phys.*, **3**, 336 (1935). [l] K. K. Kelley, *U. S. Bur. of Mines Bull.*, **406** (1937). [m] E. Terres and H. Wesemann, *Angew. Chem.*, **45**, 795 (1932). [n] P. Bix and G. Herzberg, *J. Chem. Phys.*, **21**, 2240 (1953). [o] H. Braune, S. Peter and V. Nevelling, *Z. Naturforsch*, **6a**, 32 (1951). [p] P. Goldfinger, W. Jeunehomme and B. Rosen, *Nature*, **138**, 205 (1936). *Cf.* W. Nernst and H. von Wartenberg, *Z. Elektrochem.*, **9**, 626 (1903); *Z. anorg. Chem.*, **56**, 320 (1908).

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(1) "Selected Values of Chem. Therm. Prop.," Series III, Natl. Bur. of Std., Loose Leaf, 1947–1951.

(2) P. C. Cross, *J. Chem. Phys.*, **3**, 825 (1935).

(3) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., N. Y., 1947. In a private communication Professor Gaydon states that the listed value, 5.184 e.v., should have read 5.148.

(4) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules"; 1st Edn., Prentice–Hall Book Co., N. Y., 1939; 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950.

TABLE III

CALCULATED VALUES FOR ΔH°_0 FOR THE REACTION: $^1/_2S_2 + {}^1/_2O_2 = SO$, BASED ON SPECTROSCOPIC MEASUREMENTS REPORTED IN TABLE II

ΔH°_0, kcal./mole $S + O = SO$	ΔH°_0, kcal./mole $2S = S_2$	ΔH°_0, kcal./mole $^1/_2S_2 + {}^1/_2O_2 = SO$
− 92.3	− 76	+ 4.7
− 92.3	− 83	+ 8.2
− 92.3	−101	+17.2
−118.7	− 76	−21.7
−118.7	− 83	−18.2
−118.7	−101	− 9.2

Oxygen Pressure of Iron Oxide Slags.—Larson and Chipman[5] have recently reported the results of an investigation on the activity of oxygen in iron oxide slags. As part of their study small samples of lime–iron oxide slag of varying lime content were equilibrated with gas atmospheres of varying oxygen pressure. The atmospheres used were air and CO_2–CO mixtures. The slag samples, usually 0.5 to 2.0 g., were held in platinum crucibles in a vertical tubular globar furnace with temperature control of ±1°. The furnace arrangement, which is the same as that used in the present study, is shown in Fig. 1. A steady stream of gas was passed over the slags for a sufficient time for equilibrium to be essentially realized. To further verify that equilibrium was attained some slag samples approached equilibrium from a high oxygen content while others approached from low oxygen content. Figure 2 shows the results of these experiments recalculated to express concentration as atomic per cent. of calcium in the slag. From Fig. 2 the oxygen pressure to which a lime–iron oxide slag has been exposed at 1550° can be determined if the calcium content and the ratio of ferric to total iron, j, are determined after the equilibration.

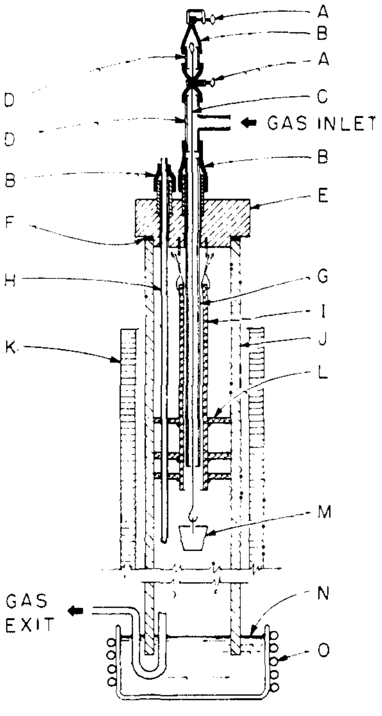

Fig. 1.—Diagram of furnace: A, clamp; B, rubber tubing; C, platinum wire; D. glass tubing; E, brass water-cooled top; F, silicone rubber gasket; G, alundum tube; H, thermocouple protection tube; I, alundum tube; J, Zircotube; K, cylindrical globar element; L, alundum radiation shields; M, crucible; N, mercury; O, water cooling coils.

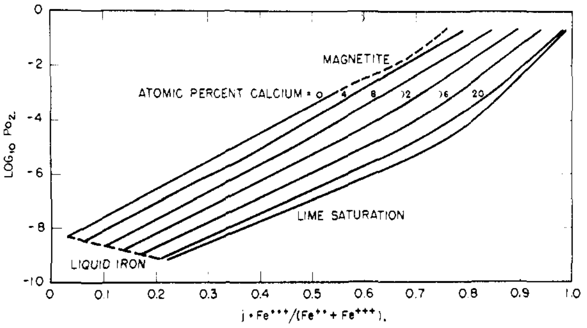

Fig. 2.—Effect of oxygen pressure on j ratio for various calcium contents at 1550°.

In addition Darken and Gurry[6] have determined the effect of p_{O_2} on j for pure iron oxide slags over a range of temperature which includes 1550°. Their results are in excellent agreement with those of Larson and Chipman.

Experimental

Apparatus.—The apparatus used by Larson and Chipman was modified slightly to accommodate the addition of SO_2 to the gas mixtures. The furnace used to equilibrate samples is the same as that shown in Fig. 1. As in their work, slag samples of 0.5 to 2.0 g. were held in platinum crucibles under a steady stream of gas, 100 to 200 ml./min., for several hours and then rapidly lowered to the bottom of the furnace where they were quenched in mercury.

Preparation and Analysis of Gas Mixtures.—Mixtures of SO_2–CO were prepared from Virginia Smelting Company "Extra Dry" liquid sulfur dioxide and Pure Company carbon dioxide. After removing traces of water vapor with anhydrone the CO_2 was passed over graphite at 1200° at which temperature the conversion to CO is nearly complete. The remaining traces of CO_2 were removed with potassium hydroxide solution and ascarite. After removing traces of water vapor from the SO_2 with phosphorus pentoxide it was mixed with the purified CO and the mixture was passed into the furnace. The ratio of SO_2 to CO could be varied by means of bleeder columns which when set at a given level held the gas flows very constant. The composition of the gas mixture entering the furnace was determined gravimetrically. Samples of the gas mixture were taken and flushed with N_2 through an analytical train consisting of an absorption bulb of ascarite, a CuO furnace at 400°, and a second absorption bulb of ascarite in series. The ratio of the weight gain in the first absorption bulb to that in the second bulb was simply converted to give the volumetric SO_2/CO ratio of the gas mixture entering the furnace.

Chemical Analysis of Slags.—The quenched samples were removed from the crucibles and crushed in a Plattner's diamond mortar to pass a 40- or 60-mesh screen with precautions to prevent oxidation. A portion of each of the slag samples was dissolved in air-free hydrochloric acid saturated with CO_2. Usually one portion of a sample was used to determine total iron, and a second portion was titrated for ferrous or ferric iron using $KMnO_4$ or $TiCl_3$. The presence of sulfur in the samples complicated the analysis because not all the sulfur evolved as H_2S when the samples were dissolved. Some of the S^{--} produced on dissolving was oxidized to elemental sulfur by ferric iron. It was necessary, therefore, to determine the amount of H_2S

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(5) H. R. Larson and J. Chipman, *J. Metals*, **5**, 1089 (1953).

(6) L. S. Darken and R. W. Gurry, THIS JOURNAL, **67**, 1398 (1945); **68**, 798 (1946).

evolved on dissolving each sample in order to correct the Fe^{+++}, Fe^{++} contents obtained from the titration analyses.

TABLE IV

SUMMARY OF EQUILIBRIUM DATA AT 1550°

Time, hr.	Final slag composition, at. % Fe^{II}	Fe^{III}	S	Ca	j	$-\log p_{O_2}$	Notes
SO_2 at 1 atm.							
2.0	4.31	20.2	0.105	20.5	0.823	3.37	a,b,d
2.0	2.26	20.2	.237	22.4	.902	2.40	d
2.0	3.60	18.85	.198	22.2	.839	3.50	d
4.0	3.34	18.1	.208	23.9	.845	3.40	d
3.5	6.55	21.5	.043	16.57	.767	3.30	
6.3	4.60	21.6	.081	18.38	.825	2.90	
4.0	10.40	23.6	.030	10.00	.695	2.82	
4.0	10.53	24.55	.028	8.90	.700	2.57	
4.0	5.85	22.9	.045	15.50	.797	2.67	
4.0	6.85	22.1	.031	15.53	.763	3.12	
18.5	20.1	23.8	.014	0.15	.542	3.14	
18.5	19.0	24.55	.017	0.36	.564	2.94	
18.5	3.21	21.6	.080	19.8	.870	2.54	d
6.0	15.9	24.8	.021	3.02	.610	2.80	
6.0	7.42	23.4	.059	13.22	.760	2.69	
13.5	13.6	24.2	.017	6.11	.641	2.74	
13.5	5.39	21.2	.051	18.3	.801	3.21	
3.0	14.33	24.05	.064	5.54	.627	2.80	
3.0	10.40	23.8	.050	9.85	.696	2.80	
2.0	8.30	23.5	.00	12.4	.739	2.80	c
15 0	9.45	22.9	.049	11;9	.708	3.04	c
$SO_2/CO = 5.50$							
4.0	13.9	16.4	6.67	15.7	0.541	5.52	c
4.0	15.8	13.87	6.25	17.0	.468	6.43	c
$SO_2/CO = 20.7$							
5.0	17.5	17.0	2.05	11.3	.492	5.30	c
5.0	12.5	17.1	2.12	16.25	.578	5.27	c
5.0	7.09	16.8	2.56	22.0	.703	5.25	c
5.0	6.56	17.12	2.36	22.0	.722	5.10	c
$SO_2/CO = 34.1$							
6.0	14.88	18.12	1.08	13.47	.549	5.11	c
6.0	8.74	17.93	1.03	18.70	.672	4.92	c
6.0	4.70	17.14	1.20	23.95	.784	4.33	c
5.0	13.15	18.50	1.35	13.80	.585	4.78	c
5.0	20.80	19.00	1.56	5.52	.477	4.45	c
5.0	3.92	13.52	1.17	29.30	.776	4.44	c
6.0	29.0	16.35	1.14	0	.362	4.88	c
6.8	17.28	17.32	1.38	11.13	.501	5.18	
6.8	9.00	17.20	1.21	19.43	.656	5.08	
6.8	23.25	17.45	1.56	5.04	.428	4.91	
11.0	9.15	16.65	1.27	20.2	.646	5.31	
11.0	16.70	17.40	1.28	10.32	.511	4.93	
11.0	22.45	15.20	1.46	6.62	.404	5.42	
15.1	30.55	15.05	1.55	0	0.330	5.20	
10.2	10.22	17.52	1.34	17.89	.631	5.05	
$SO_2/CO = 42.3$							
5.0	15.30	17.70	0.96	12.70	.537	5.07	
5.0	11.77	17.58	.80	16.42	.598	5.12	
13.7	7.03	18.77	.66	19.70	.728	4.36	
6.5	29.25	14.58	.96	0	.333	5.16	
6.5	19.10	17.13	.94	9.57	.473	5.20	
5.9	4.75	15.62	1.00	25.80	.768	4.52	

[a] $j = Fe^{+++}/(Fe^{+++} + Fe^{++})$. [b] Brackets indicate samples were equilibrated simultaneously. [c] Sulfur by gravimetric analysis, all others by combustion. [d] Data marked 1 to 5 in Fig. 3, excluded from averages of Table V.

The sulfur contents were determined by two different methods: combustion of the slag with CO_2 to remove the sulfur as SO_2 and titration of this SO_2 with KIO_3; and gravimetric determination through the precipitation of sulfur as $BaSO_4$.

In addition several of the samples were analyzed for calcium content; however, the analyses were always sufficiently accurate to warrant the calculation of the calcium and oxygen contents from the analysis of ferric, ferrous iron and sulfur present in the slag.

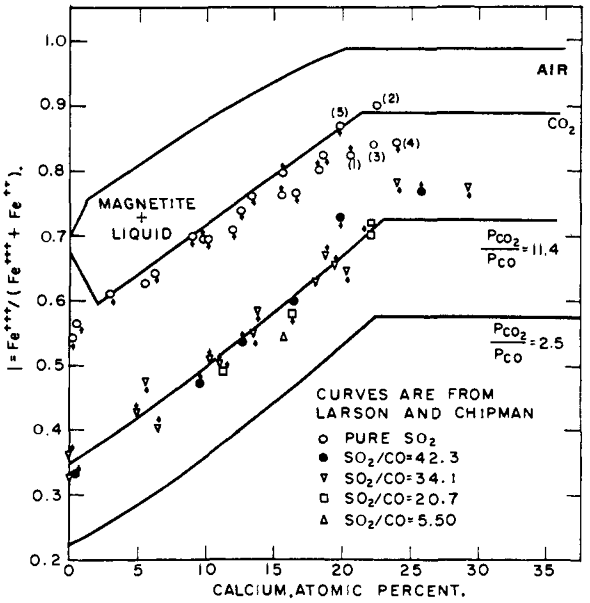

Fig. 3.—Effect of gas and melt compositions on ratio, $j = Fe^{+++}/(Fe^{+++} + Fe^{++})$.

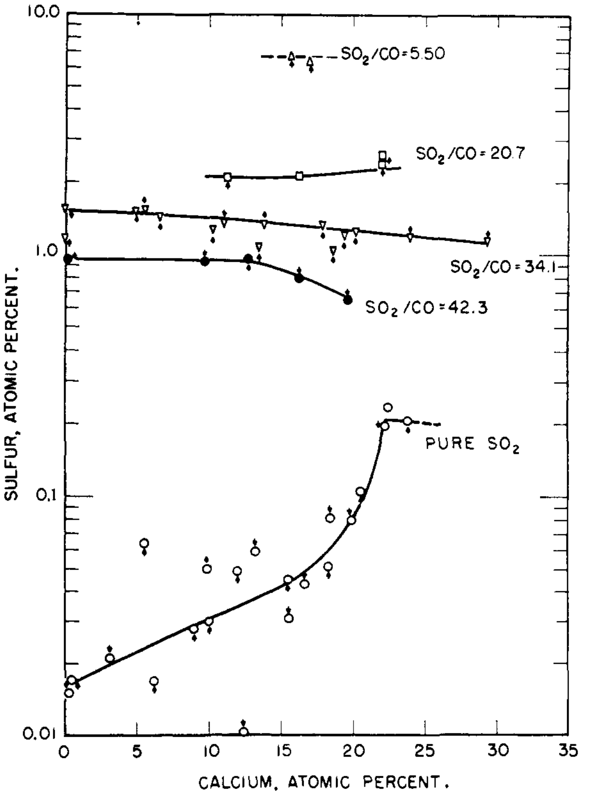

Fig. 4.—Effect of calcium on sulfur content of Ca–Fe–O melts at 1550°.

TABLE V

CALCULATED GAS COMPOSITIONS AT 1550°

Gas mixture	$-\log p_{O_2}$	Std. dev., σ	p_{O_2}	p_{CO}	p_{CO_2}	p_{S_2}	p_{SO_3}
Pure SO_2	2.89	0.20	1.29×10^{-3}	....	....	4.49×10^{-8}	4.25×10^{-4}
SO_2/CO = 42.3	4.91	.33	1.23×10^{-5}	1.64×10^{-3}	2.15×10^{-2}	4.51×10^{-4}	3.97×10^{-5}
SO_2/CO = 34.1	4.92	.32	1.20×10^{-5}	2.05×10^{-3}	2.64×10^{-2}	4.66×10^{-4}	3.86×10^{-5}
SO_2/CO = 20.7	5.23	.08	5.88×10^{-6}	4.60×10^{-3}	4.15×10^{-2}	1.81×10^{-3}	2.8×10^{-5}
SO_2/CO = 5.50	5.52	..	3.02×10^{-6}	2.06×10^{-2}	0.1334	4.27×10^{-3}	1.5×10^{-5}

Gas mixture	$-\log p_{O_2}$	Std. dev., σ	p_{SO_2}	p_{SO}	p_{COS}	p_S	p_O
Pure SO_2	2.89	0.20	0.998	3.00×10^{-3}	....	2.1×10^{-6}	6.0×10^{-6}
SO_2/CO = 42.3	4.91	.33	.956	1.97×10^{-2}	1.1×10^{-6}	2.1×10^{-4}	5.8×10^{-7}
SO_2/CO = 34.1	4.92	.32	.946	2.45×10^{-2}	1.4×10^{-6}	2.2×10^{-4}	5.8×10^{-7}
SO_2/CO = 20.7	5.23	.08	.916	3.43×10^{-2}	6.0×10^{-6}	4.3×10^{-4}	4.0×10^{-7}
SO_2/CO = 5.50	5.52	..	.721	0.1163	4.1×10^{-5}	6.6×10^{-4}	2.9×10^{-7}

Results

Table IV summarizes the results of the experimental work at 1550°. The last column in Table IV is p_{O_2} for equilibrium with each slag composition according to Fig. 2 which is based on sulfur-free slags. Figures 3 and 4 show the variation of j and atomic per cent. sulfur with calcium content for each atmosphere. The variation of calcium content is not important for the purpose of this investigation; however, it forms a necessary part of a study of the sulfur equilibrium between slags and gas atmospheres. It can be seen that for a given atmosphere the sulfur contents do not vary greatly with calcium content. The sulfur content of the slags must be given attention because it is possible that the substitution of sulfur atoms for oxygen atoms alters the relation between j and calcium content for a given p_{O_2}. This possibility will be examined in a later section.

The first two columns of Table V are the average values of log p_{O_2} and the standard deviation, respectively, for each of the atmospheres investigated. The points marked 1 to 5 in Fig. 3 and Table IV have been omitted from the calculation of the average value of log p_{O_2} for pure sulfur dioxide. These points, all lying near lime saturation, scatter quite badly and are less accurate than points lying along the lower portion of the curve. The value of j given by the intercept of the pure SO_2 curve at 0% calcium is 0.545. From Darken and Gurry's work this gives a value of −2.85 for log p_{O_2} which is in excellent agreement with the average reported in Table V. From the two determinations with a gas atmosphere of SO_2/CO = 5.50, the first is given preference over the second because its final composition differed only insignificantly from the charge composition, whereas the second was charged at a much lower ferric content and obviously did not reach equilibrium.

Treatment of Results

Using sulfur, carbon and oxygen balances in the gas phase, the value of p_{O_2} determined from slag compositions, and the known equilibrium relations

$$p_{SO_2}/(p_{S_2}{}^{1/2}p_{O_2}) = 3.66 \times 10^6$$

$$p_{CO_2}/(p_{CO}p_{O_2}{}^{1/2}) = 3.72 \times 10^3$$

$$p_{SO_3}/(p_{SO_2}p_{O_2}{}^{1/2}) = 1.18 \times 10^{-2}$$

the gas composition resulting from the gas phase reactions of the gas mixture entering the furnace were calculated on the basis of the following gas species being present: SO_3; SO_2; S_2; SO; CO_2; CO; O_2. The results are summarized in Table V. Only the monomeric form of sulfur monoxide is considered; it will be shown later that the data exclude polymeric forms under the experimental conditions. The validity of omitting COS, S and O as important gas components was checked using the following equilibrium relations which are based on the data of Tables I and II using the value of ΔH_0° finally selected for dissociation of S_2

$$p_{COS}/(p_{CO}p_{S_2}{}^{1/2}) = 3.06 \times 10^{-2}$$

$$p_{O_2}/p_O{}^2 = 3.61 \times 10^7$$

$$p_{S_2}/p_S{}^2 = 9.8 \times 10^3$$

The pressures of COS, S and O that would develop for the gas mixtures used are included in Table V where it can be seen that their omission does not introduce any appreciable error in the sulfur and oxygen balances. The pressure of CS, S_4, S_6 and S_8 have also been calculated and found to be negligibly small.

TABLE VI

CALCULATION OF EQUILIBRIUM CONSTANTS AND THE HEAT OF FORMATION OF SO FROM S_2 AND O_2

Gas mixture	$K_1 \times 10^{-3}$ 1823°K.	$K_2 \times 10^{-2}$ 1823°K.	$^1/_2S_2 + {}^1/_2O_2 = SO$ ΔF° 1823	ΔH°_0, cal.
Pure SO_2	9.2	3.94	−21,600	−19,300 ± 1600
SO_2/CO = 42.3	13.9	2.66	−20,200	−17,900 ± 2700
SO_2/CO = 34.1	11.1	3.27	−21,000	−18,700 ± 1200
SO_2/CO = 20.7	11.0	3.33	−21,100	−18,800 ± 1200
SO_2/CO = 5.50	3.57	10.25	−25,100	−22,800

$$K_1 = \frac{p_{SO_2}}{p_{SO}p_{O_2}{}^{1/2}} \qquad K_2 = \frac{p_{SO}}{p_{S_2}{}^{1/2}p_{O_2}{}^{1/2}}$$

TABLE VII

RECOMMENDED VALUES OF THERMODYNAMIC PROPERTIES

KCAL.

	ΔH°_0	ΔF°_{1823}	$\Delta F^\circ_{298.16}$
$2S = S_2$	− 83	−33	− 76
$S + O = SO$	−118.7	−69.2	−112.2
$^1/_2S_2 + {}^1/_2O_2 = SO$	− 18.2	−20.6	− 18.6
$SO + {}^1/_2O_2 = SO_2$	− 67.5	−34.1	− 62.7

From the calculations summarized in Table V, the heat of formation of SO from S_2 and O_2 was determined as shown in Table VI. The results are in reasonable agreement for each atmosphere with the exception of SO_2/CO = 5.50; however, since there was only one determination for SO_2/CO = 5.50 the other four atmospheres are to be emphasized. Since there is more than one order of magnitude difference in the sulfur contents of the slags for the atmospheres pure SO_2 and SO_2/CO = 20.7, the results of Table VI indicate that there is no major effect on the relation between j and the calcium content when S atoms replace oxygen atoms in the slag up to at least two atomic per cent. sulfur. Also the results eliminate the possibility of appreciable amounts of polymeric forms of SO being present under the experimental conditions because their presence would have prevented the agreement reported in Table VI.

The average of ΔH°_0 for the first four atmospheres listed in Table VI is −18.7 kcal./mole. Referring to Table III it can be seen that a clear choice for the heats of formation of SO and S_2 from the atoms is indicated. The combination of the high heat of formation of SO with the intermediate heat of formation of S_2 results in a heat of formation of SO from S_2 and O_2 of −18.2 kcal./mole. These selected data lead to the recommended values of ΔH°_0, $\Delta F^\circ_{298.16}$ and ΔF°_{1823} for the reactions involved in the thermal dissociation of sulfur dioxide presented in Table VII.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 41 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Nitromethane: The Vapor Heat Capacity, Heat of Vaporization, Vapor Pressure and Gas Imperfection; the Chemical Thermodynamic Properties from 0 to 1500°K.

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Because nitromethane is important both as an industrial chemical and, from a theoretical standpoint, as the simplest member of the family of nitroparaffins, measurements were made of several of its thermodynamic properties. The properties studied were: (1) the vapor pressure at 15 temperatures from 55 to 136° [$\log_{10} p(\text{mm.}) = 7.28050 - 1446.186/(t + 227.515)$; t in °C.]; (2) the heat of vaporization at 4 temperatures from 318 to 374°K. [$\Delta H_v = 11{,}730 - 4.9977\,T - 1.2400 \times 10^{-2}T^2$ cal. mole^{-1}]; and (3) the vapor heat capacity at 2 to 4 pressures at each of 6 temperatures from 363 to 523°K. [$C^\circ_p = 2.352 + 4.2882 \times 10^{-2}\,T - 1.694 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1}]. The observed effects of gas imperfection on the thermodynamic properties were correlated with the equation of state, $PV = RT(1 + B/V)$, where $B = -300 - 12.97 \exp(1700/T)$ cc. mole^{-1}. The results of these studies and the entropy and heat of formation data reported by other investigators provide relatively complete and highly accurate experimental thermodynamic data for nitromethane. These data form a sound basis for computing the chemical thermodynamic properties by appropriate methods of statistical mechanics and thermodynamics. Values of the following properties were computed at selected temperatures from 0 to 1500°K.: $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, S°, C°_p, ΔH°_f, ΔF°_f and $\log_{10} K_f$.

Because of the importance of nitromethane as an industrial chemical, and because of its importance in theoretical considerations as the simplest member of the nitroparaffin family, many investigations have been made of its physical and chemical properties. Measurements of properties related to the subject matter of this paper include determinations of the vapor heat capacity,[1,2] the heat of vaporization,[1,3-5] the vapor pressure,[5-8] the vapor density,[1,9,10] the entropy at 298.16°K.,[5] and the heat of formation at 298.16°K.[8,11] The present investigation was made to provide more accurate and extensive values of the chemical thermodynamic properties of nitromethane. The experimental studies consisted of determinations of: (1) the vapor pressure at 15 temperatures from 55 to 136°; (2) the heat of vaporization at 4 temperatures from 318 to 374°K.; and (3) the vapor heat capacity at 2 to 4 pressures at each of 6 temperatures from 363 to 523°K. The heat capacity in the ideal gaseous state and an equation of state for the real vapor were obtained from the experimental results. These thermodynamic data, the value of the entropy reported by Jones and Giauque,[5] and the value of the standard heat of formation reported by Prosen[11] were used with available spectroscopic and molecular structure information in calculations of the chemical thermodynamic properties of nitromethane at selected temperatures from 0 to 1500°K.

Experimental

Physical Constants.—All data reported in this paper are based on a molecular weight of 61.042 for nitromethane and the following definitions: 0°C. = 273.16°K.; 1 cal. = 4.1840 abs. j. = 4.1833 int. j. The 1951 International Atomic Weights[12] and the 1951 values of the fundamental physical constants[13] were used for all computations.

The Material.—The sample of nitromethane used in these experiments was obtained by chemical and physical purification of a sample donated by the Commercial Solvents Corporation, Terre Haute, Indiana. The method of purification employed and some physical properties of the purified sample were described elsewhere.[14] Before use in the experimental studies, the sample was dried by passing the vapors through $Mg(ClO_4)_2$. The purity of the sample, as determined by the time-temperature freezing-point method,[15] was 99.9 mole %. That impurities of different volatility were not present in significant quantities was verified in the vapor pressure study by the observation that the difference in the boiling and condensation temperatures of the sample was only 0.006° at 760 mm. pressure. However, it was necessary to reflux the sample in the ebulliometer for about 2 hours before the difference was reduced to

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