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CALCULATION OF PARTIAL PRESSURES ON EACH SULFUR SPECIES IN TOTAL SULFUR VAPOR AT TEMPERATURES FROM 350° TO 1000°C UNDER ONE ATMOSPHERIC PRESSURE

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The partial pressures of S_2, S_3, ---- S_8 in total sulfur vapor under one atmospheric pressure were calculated by reconsidering literature data. The total sulfur pressure consists mainly of the species of S_2 at the temperature ranges higher than 650°C. At lower temperatures S_7 species besides S_8 and S_6 becomes important constituent in sulfur vapor.

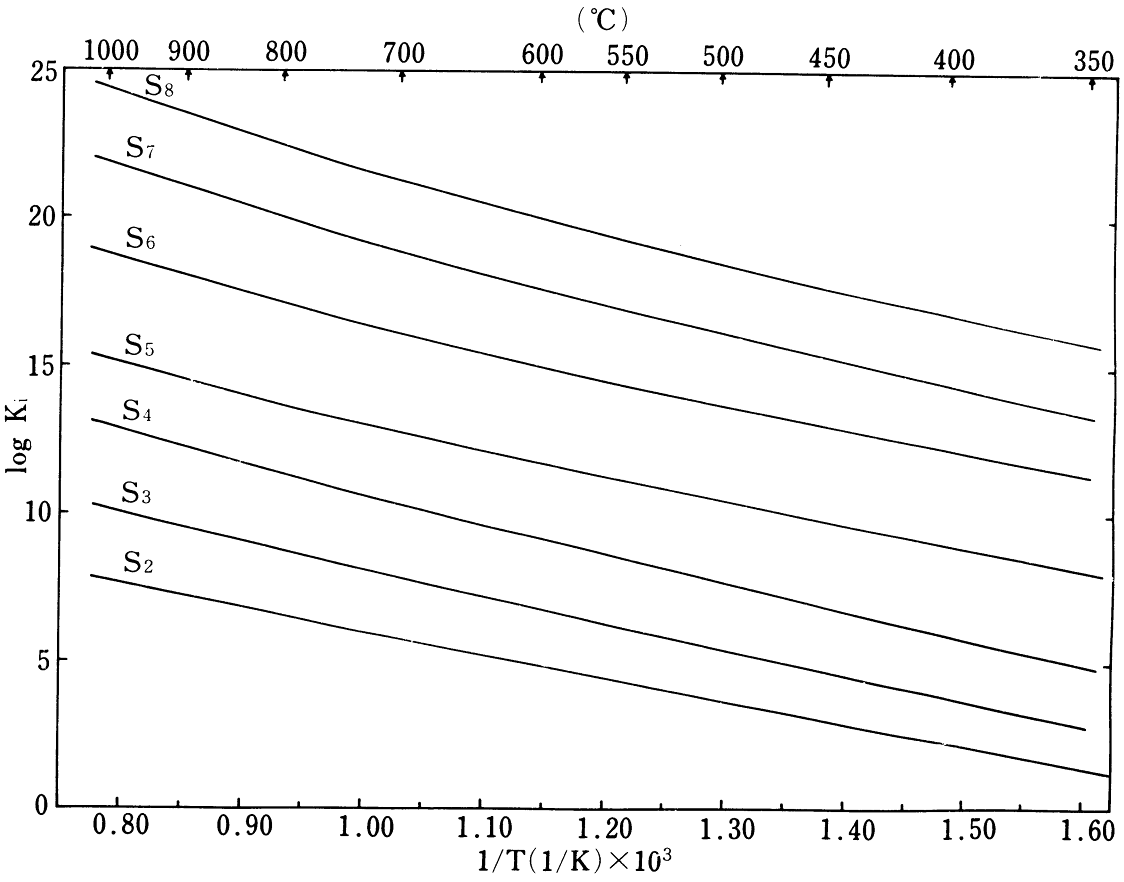
When we estimate the thermodynamic functions at a chemical reaction related to the sulfur vapor at higher temperatures and at lower pressures, we usually represent a partial pressure of S_2 species as a gaseous component. However, we have to take into account the appreciable amounts of different species besides S_2 especially in the condition at lower temperatures and at higher pressures. In such a case we need a correction to the partial pressure Ps_2 to evaluate an accurate thermodynamic function (viz. the standard free energy of a reaction related to the sulfur pressure etc.). In spite of the importance of the correction it is rather difficult experimentally to distinguish each partial pressure from total sulfur vapor. For example, the mass spectrometric studies still do not give us satisfactory results about the problem. A better approach to evaluate the correction seems to apply some reliable thermodynamic data in literatures.

Recently, authors have developed a new apparatus$^{1)}$ for sulfur vapor pressure control which works effectively at higher sulfur pressures(~10^{-4}∿~1 atm) and at temperatures between ∿400° and ∿1000°C under 1 atm. The apparatus can be used to synthesize so many metal sulfides and to study the thermodynamic equilibria of these compounds. Even in the studies by any other methods such as an experiment of hydrothermal sulfide system which is carried out at higher sulfur pressures, the correction to Ps_2 will be needed on the results obtained, if we want to get more precise thermodynamic data.

Since we are lacking reliable data on the partial pressures of different sulfur species in sulfur vapor at relatively higher total sulfur pressures under atmospheric condition, we will present here the partial pressures on each species in total sulfur pressure and also will describe the calculation of the corrected Ps_2 in total sulfur pressure at temperatures between 350° and 1000°C under 1 atm from reconsideration of a few reliable literature data already published.

It is well known that sulfur vapor consists of the species from S_1 to S_8 in equilibrium. The stability between S_1 and S_2 was investigated by Budininkas et al$^{2)}$. From their results the existence of S_1 species could be negligible at temperatures below 1500 K so that it may be enough to consider the species from S_2 to S_8 under the present condition. Braune et al.[3)] measured vapor pressures of sulfur at sulfur pressures from $10^{-1.5}$ to about 1 atm and at temperature ranges from 350 up to 1273 K, and then determined the mean molar mass at each sulfur pressure and also calculated the partial pressures on each sulfur species by assuming the existence of only even species, i.e. S_2, S_4, S_6, and S_8. Nesmeyanov[4)] compiled vapor pressure of liquid sulfur and sulfur partial pressures of only even species at temperatures below 540°C. Their results ignoring odd species, however, would not express real partial pressures because of the existence of the appreciable amounts of odd species in sulfur vapor. Drowart et al[5)] measured the sulfur species using the mass spectrometer connected with a Knudsen cell at temperatures between 200° and 400°C. Unfortunately, the accurate measurement by use of this method is restricted to the pressures below about 10^{-3} atm and temperatures below about 400°C. Rau et al.[6)] measured sulfur vapor pressures from about 1 atm up to about 140 atm at temperatures between 823 and 1273 K using quartz-made Bourdon gage and calculated the partial pressures of all sulfur species from S_2 to S_8 mostly based on their own data newly summarized. The thermodynamic data on each sulfur species obtained by Rau et al. seem to be most reliable for the present because the precise measurement by Bourdon gage usually gives us good vapor pressure data. Since they obtained almost all data of vapor pressure of sulfur

Fig. 1 Calculated equilibrium constants of the formation on each sulfur species from the thermodynamic data of Rau et al. at temperatures between 350° and 1000°C.



above 1 atm, it is impossible to calculate each sulfur partial pressure from their own data at vapor pressures lower than about 1 atm. If we use the thermodynamic data of Rau et al.[6)] on each sulfur species together with the data of Braune et al.[3)] on the total sulfur pressure and the mean molar mass, it will become possible to estimate all sulfur partial pressures on each sulfur species at sulfur vapor pressures below 1 atm under 1 atmospheric pressure.

Fig. 1 shows the relationship between the equilibrium constants of the formation on each sulfur species K_i calculated from the thermodynamic data of Rau et al.[6)] and reciprocal absolute temperature. Here it is assumed that sulfur vapor behaves like ideal mixtures of the different species. The equilibrium reaction between S_2 and all the other species from S_3 to S_8 is represented below;

$$S_i = i/2\ S_2 \qquad\text{-----------}\ (1)$$

where i indicates integers from 3 to 8. The equilibrium constant of Eq.(1), K_i', is given by the following relations;

$$K_i' = K_2{}^{i/2}/K_i = Ps_2{}^{i/2}/Ps_i \qquad\text{-----------}\ (2)$$

where Ps_i is a partial pressure of i species. As already described by Braune et al.[3)] we have another relation between the partial pressures and total sulfur pressure as follows;

$$\sum_{i=2}^{8} i\ Ps_i = \nu P_t \qquad\text{-----------}\ (3)$$

where ν and P_t represent the mean molar mass and a total sulfur pressure, repectively. From Eqs.(2) and (3), we can derive another relation;

$$\sum_{i=2}^{8} i\ Ps_2{}^{i/2}/K_i' = \nu P_t \qquad\text{-----------}\ (4)$$

A combination of two sets of data in a computer program, one is the values of ν and P_t of Braune et al.[3)] and the other is K_i' calculated from the data of Rau et al.[6)], allows us to calculate the partial pressure Ps_2 from Eq.(4).

The relation between the partial pressure Ps_2 and P_t calculated is illustrated in Fig. 2. As shown in Fig. 2, at the temperatures above 650°C S_2 species are predominant in total sulfur vapor, while at the temperatures below 500°C the amount of S_2 species in total sulfur vapor decreases with decreasing temperature. The dashed lines represent the Ps_2 in P_t estimated from the data of Braune et al. in which only even species were assumed. At the temperatures below 450°C slight discrepancy between the present results and those of Braune et al. is seen as illustrated in Fig. 2. It may refer to the contribution of odd species as described later on. At the temperatures above 500°C no appreciable discrepancy is identified on both results. This means that two sets of Ps_2 values, one is obtained by Braune et al. at lower sulfur pressures and the other is calculated from the data obtained by Rau et al. at pressures higher than about 1 atm, are related with good agreement. According to Braune et al., the precision of P_t, T, and ν are quite good. For example, P_t and T are to

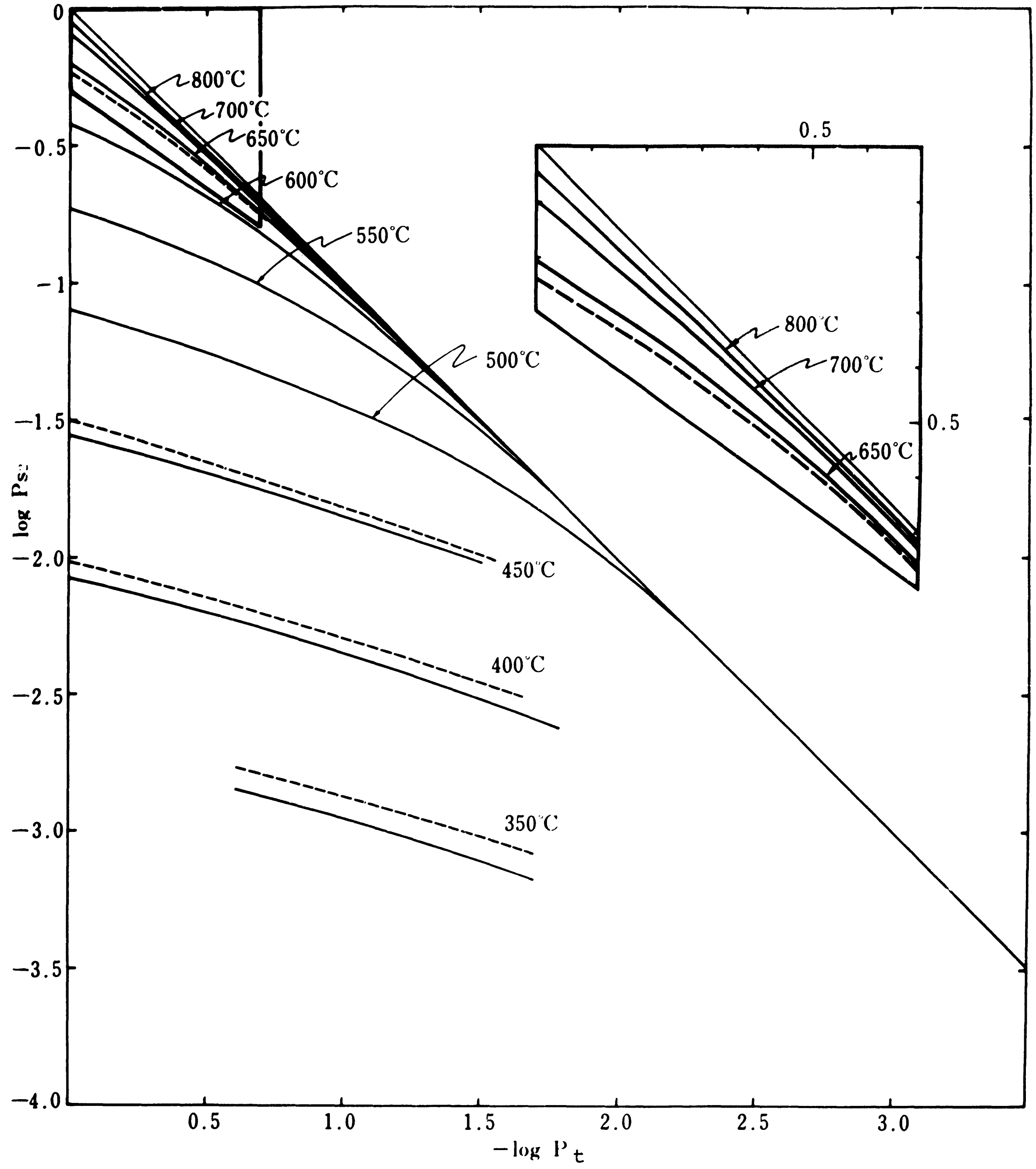


Fig. 2. Partial pressure Ps_2 in total sulfur pressure P_t calculated from Eq.(4) using K_i' estimated from the data of Rau et al., and ν and P_t obtained by Braune et al.

be within 0.5% and 0.2%, respectively and ν is about 1%. However, it is rather difficult to estimate the precision of Ps_2 calculated from Eq.(4) because Eq.(4) containes K_i' term which is calculated from many thermodynamic sources. In spite of the difficulty of the estimation of accuracy in K_i' the good agreement between the present Ps_2

Table 1. Partial Pressures on Each Sulfur Species at Some Temperatures under 1 atm.

Total Sulfur Pressure $-\log P_t$	$-\log Ps_2$	$-\log Ps_3$	$-\log Ps_4$	$-\log Ps_5$	$-\log Ps_6$	$-\log Ps_7$	$-\log Ps_8$
350°C							
1.483	3.097	3.850	4.028	3.031	1.986	2.128	1.915
1.211	3.015	3.726	3.863	2.825	1.738	1.840	1.584
1.091	2.980	3.674	3.794	2.738	1.634	1.718	1.446
0.996	2.953	3.633	3.739	2.670	1.552	1.623	1.337
0.901	2.926	3.592	3.685	2.602	1.471	1.528	1.229
0.851	2.912	3.572	3.658	2.568	1.429	1.480	1.173
0.735	2.879	3.522	3.591	2.485	1.330	1.364	1.041
400°C							
1.411	2.480	3.261	3.498	2.811	1.896	2.051	1.997
1.151	2.395	3.133	3.328	2.598	1.640	1.752	1.655
1.033	2.358	3.079	3.256	2.508	1.532	1.626	1.511
0.939	2.330	3.037	3.199	2.437	1.447	1.527	1.398
0.847	2.302	2.995	3.143	2.367	1.363	1.429	1.286
0.796	2.288	2.973	3.114	2.331	1.320	1.397	1.228
0.683	2.254	2.922	3.047	2.247	1.219	1.260	1.093
0.383	2.167	2.791	2.873	2.029	0.957	0.956	0.725
0.258	2.131	2.738	2.801	1.939	0.850	0.830	0.602
450°C							
1.323	1.963	2.775	3.069	2.654	1.857	2.027	2.116
1.067	1.869	2.635	2.882	2.420	1.576	1.700	1.742
0.952	1.833	2.580	2.809	2.329	1.467	1.573	1.596
0.865	1.803	2.535	2.749	2.255	1.378	1.468	1.477
0.780	1.774	2.492	2.691	2.182	1.290	1.366	1.360
0.727	1.758	2.469	2.660	2.144	1.244	1.313	1.299
0.618	1.724	2.417	2.591	2.057	1.140	1.192	1.161
0.325	1.633	2.281	2.410	1.831	0.870	0.876	0.800
0.203	1.597	2.227	2.337	1.740	0.760	0.748	0.653
500°C							
1.200	1.536	2.388	2.741	2.575	1.891	2.086	2.310
0.952	1.430	2.228	2.528	2.308	1.571	1.713	1.884
0.877	1.398	2.181	2.465	2.229	1.476	1.602	1.757
0.847	1.388	2.165	2.444	2.203	1.445	1.566	1.715
0.765	1.355	2.116	2.379	2.129	1.348	1.452	1.585
0.682	1.324	2.070	2.317	2.044	1.254	1.343	1.460
0.633	1.306	2.042	2.280	1.998	1.199	1.279	1.387
0.534	1.271	1.989	2.210	1.910	1.094	1.156	1.247
0.256	1.176	1.848	2.021	1.674	0.810	0.826	0.869
0.140	1.139	1.791	1.946	1.580	0.697	0.694	0.718
600°C							
0.915	0.986	1.978	2.504	2.822	2.400	2.710	3.231
0.681	0.804	1.706	2.142	2.369	1.856	2.075	2.506
0.603	0.752	1.627	2.037	2.237	1.698	1.891	2.296
0.583	0.736	1.604	2.006	2.199	1.653	1.838	2.235
0.521	0.698	1.547	1.929	2.103	1.537	1.703	2.080
0.432	0.643	1.465	1.820	1.967	1.374	1.512	1.863
0.391	0.621	1.431	1.775	1.911	1.307	1.434	1.773
0.299	0.571	1.356	1.675	1.785	1.156	1.259	1.573
0.056	0.453	1.179	1.439	1.490	0.802	0.846	1.101
0.012	0.428	1.141	1.388	1.427	0.726	0.757	0.999
800°C							
0.746	0.759	2.235	3.283	4.572	4.801	5.549	6.774
0.451	0.475	1.808	2.715	3.861	3.948	4.555	5.637
0.363	0.387	1.677	2.539	3.642	3.685	4.248	5.286
0.328	0.358	1.633	2.481	3.569	3.598	4.146	5.169
0.237	0.264	1.493	2.294	3.335	3.317	3.818	4.795
0.140	0.174	1.357	2.113	3.109	3.046	3.501	4.433
0.091	0.126	1.286	2.018	2.991	2.903	3.335	4.243
0.021	0.020	1.125	1.804	2.723	2.582	2.961	3.816
1000°C							
0.666	0.673	2.511	3.943	5.924	6.625	2.699	9.430
0.368	0.384	2.077	3.364	5.200	5.756	6.686	8.272
0.276	0.291	1.938	3.179	4.969	5.479	6.362	7.902
0.245	0.261	1.892	3.118	4.893	5.387	6.255	7.781
0.149	0.165	1.748	2.926	4.652	5.099	5.919	7.396
0.053	0.070	1.605	2.735	4.414	4.813	5.585	7.015

evaluated by Eq.(4) and Ps_2 obtained by Braune et al. at higher temperatures may suggest that K_i or K_i' estimated from the data of Rau et al. is quite reliable. Accordingly, we suppose that the uncertainty of the present Ps_2 obtained may be less than a few per cent in logarithmic indication. In the temperature ranges below 450°C we can not estimate Ps_2 in P_t at total sulfur pressures lower than $10^{-1.8}$ atm because of lack of the data from the experimental difficulty to measure lower sulfur vapor pressures. Ps_2 in total sulfur at higher pressures and at the temperatures above 650°C is shown in another wedge-shaped square extended two times in scale in Fig. 2.

We may evaluate all the other species besides S_2 using Eq.(2). The data obtained at several temperatures are summarized in Table 1. As given in Table 1, it seems that S_7 besides S_8 and S_6 species are important at lower temperatures, while at higher temperatures S_2 are dominant in all species and second important are S_3. Accordingly, the present results estimated may be more reliable than those of Braune et al.$^{3)}$, especially at lower temperatures below 450°C.

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