BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2411—2414 (1966)

The Chemical Equilibrium of the $2H_2S+SO_2=3S+2H_2O$ Reaction in Solfataras of the Nasudake Volcano

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(Received February 7, 1966)

The stability of native sulfur in solfataras depends upon the temperature, the pressure, and the chemical composition of the solfataric gases with which native sulfur is in equilibrium. The equilibrium constant of the $2H_2S+SO_2=3S_{(s,l)}+2H_2O$ reaction may be expressed as:

$$K = \frac{X^2_{H_2O}}{X^2_{H_2S}X_{SO_2}P},$$

where X is the mole fraction of the gaseous components in the system and where P is the total pressure on the system. By the use of this relationship, the equilibrium temperature of natural solfataric gases with respect to the reaction may be estimated, provided the theoretical value of K, the chemical composition, and the pressure of natural solfataric gases are known. The attainment of chemical equilibrium of the reaction in solfataric gases of the Nasudake Volcano has been examined by comparing the estimated equilibrium temperature with the observed outlet temperature of the solfataras. The results indicate that the native sulfur occurring in the solfataras is approximately in equilibrium with the solfataric gases. On this basis, an attempt has also been made to explain the behavior of hydrogen sulfide and sulfur dioxide in solfataric gases.

Many investigators have discussed the chemistry of volcanic gases in terms of thermodynamics. Ellis(1) made comprehensive thermodynamic calculations on the variation in the chemical composition of volcanic gases with the temperature and with the pressure. Krauskopf(2) also made thermodynamic calculations on the feasibility of the vapor transportation of heavy metals in magmatic vapor. Recently, Matsuo(3) presented similar calculations with relevance to the possibility of a heterogeneous reaction in magma effecting the creating of volcanic gases.

On the other hand, the thermodynamics were applied to interpreting the results from the analyses of natural volcanic gases by Oana(4) and by Matsuo(5). Their studies showed that, in high-temperature volcanic gases, the chemical equilibrium is seemingly established, at least with respect to the $3H_2+SO_2=H_2S+2H_2O$ and $CO+H_2O=CO_2+H_2$ reactions.

In the present paper, the authors will attempt to extend the application of thermodynamics to the heterogeneous reaction, $2H_2S+SO_2=3S_{(s,l)}+2H_2O$, in natural solfataras. The authors wish to examine the attainment of chemical equilibrium in solfataric gases during its ascent toward the surface. In addition, it is important to consider the effect of the chemical equilibrium of the reaction upon the hydrogen sulfide and sulfur dioxide portions of solfataric gases.

Results and Discussion

The Character of Solfataric Gases of the Nasudake Volcano.—Mizutani, Sugiura and Oana(6) analyzed solfataric gases of the Nasudake Volcano, Tochigi, Japan, and found some correlation between the temperature of the solfataras and the behavior of the major chemical components of the gases. For example, there is a notable increase in the amounts of hydrogen sulfide and sulfur dioxide in the temperature range between 100 and 200°C when the amount of the sulfur compounds in the gases is plotted against the outlet temperature of the solfataras. This finding led the present authors to conclude that the major part of the sulfur compounds in the gases at temperatures between 100 and 200°C was contributed secondarily by subterranean native sulfur accumulated through previous solfataric activities of this volcano. There is also a trend toward an increase in the ratio of hydrogen sulfide to sulfur dioxide in the gases with a lowering of the temperature.

In this solfataric area, native sulfur is mined by introducing solfataric gases into artificial gas channels, where native sulfur is then deposited as the

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1) A. J. Ellis, *Am. J. Sci.*, **255**, 416 (1957).
2) K. B. Krauskopf, *Econ. Geol.*, **52**, 786 (1957).
3) S. Matsuo, *J. Earth Sci. Nagoya Univ.*, **8**, 222 (1960).
4) S. Oana and K. Takahashi, *Geol. Survey Japan, Report*, **170**, 115 (1957).
5) S. Matsuo, *J. Earth Sci. Nagoya Univ.*, **9**, 80 (1961).
6) Y. Mizutani, T. Sugiura and S. Oana, Read at the Meeting of the Volcanological Society of Japan, October 1961.

temperature falls. Small pools of liquid sulfur are usually found at the openings of gas channels.

The Chemical Equilibrium of the $2H_2S+SO_2=3S+2H_2O$ Reaction.—In solfataras, native sulfur usually occurs in three different forms: rhombic, monoclinic, and liquid, depending on the temperature. Therefore, the following three reactions must be considered:

$$2H_2S + SO_2 = 2H_2O + 3S_{(rh.)}, \quad \text{for } T<95.6°C \qquad (1)$$

$$2H_2S + SO_2 = 2H_2O + 3S_{(mono.)}, \quad \text{for } T=95.6\text{—}119°C \qquad (2)$$

$$2H_2S + SO_2 = 2H_2O + 3S_{(s,l)}, \quad \text{for } T>119°C \qquad (3)$$

The appearance or disappearance of native sulfur in solfataras may be controlled by the temperature, the total pressure, and the chemical composition of the gases in equilibrium with the native sulfur. The equilibrium constants of these reactions may be expressed as:

$$K = \frac{X^2_{H_2O}}{X^2_{H_2S}X_{SO_2}P} \qquad (4)$$

where K is the equilibrium constant, X is the mole fraction of the gaseous components in the system, and P is the total pressure on the system.

The theoretical equilibrium constant for these reactions may be calculated from the free-energy change for these reactions by using the $\ln K=-\Delta F/\boldsymbol{R}T$ relation, where ΔF is the free-energy change, $\boldsymbol{R}$ is the gas law constant, and T is the absolute temperature of the system. The values of the free-energy change for these reactions may be obtained from the thermodynamic data given by Kubaschewski and Evans⁷⁾ and Rossini et al.⁸⁾ The temperature functions of the equilibrium constant obtained are:

for Reaction 1:

$$\log K_1 = -11.43 + 0.333 \log T + 1.53\times10^{-3}\, T + 7720\, T^{-1} + 1.73\times10^4\, T^{-2} \qquad (5)$$

for Reaction 2:

$$\log K_2 = -11.35 + 0.302 \log T + 1.76\times10^{-3}\, T + 7690\, T^{-1} + 1.73\times10^4\, T^{-2} \qquad (6)$$

and for Reaction 3:

$$\log K_3 = -18.90 + 3.09 \log T + 1.28\times10^{-3}\, T + 7900\, T^{-1} + 1.73\times10^4\, T^{-2} \qquad (7)$$

The relation between the equilibrium constant and the temperature obtained from these equations is shown in Fig. 1.

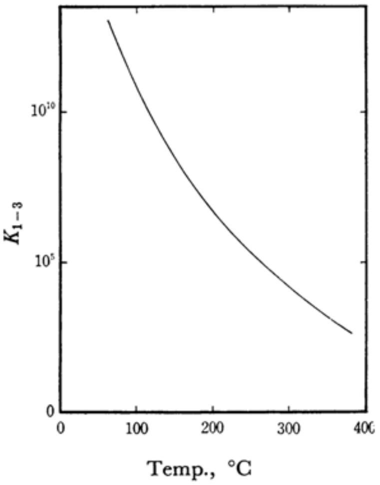

Fig. 1. Relation between equilibrium constant and temperature with respect to reaction $2H_2S+SO_2=3S_{(s,l)}+2H_2O$.

By the use of these relations, the equilibrium temperature of natural solfataric gases with respect to the above reactions may be estimated from the observed value of K. For solfataric gases of the Nasudake Volcano the observed value of $X^2_{H_2O}/X^2_{H_2S}X_{SO_2}$ may be obtained from the analytical data of the gases given by Mizutani et al.⁹⁾ Some examples of the data are given in Table I. The observed values of $X^2_{H_2O}/X^2_{H_2S}X_{SO_2}$ thus obtained are given in Table II. The equilibrium temperature of the solfataric gases may be estimated from these values, provided the total pressure on the system is known. The total pressure of the gases is assumed to be 1 atm. for the first approximation, because the gases are emitted from openings of gas channels with a rather low static pressure (close to 1 atm.).¹⁰⁾ The equilibrium temperatures thus estimated are given in Table II.

By comparing the estimated equilibrium temperatures with the observed outlet temperatures, the degree of the attainment of the chemical equilibrium of the reaction at the outlet of the solfataras may be examined. As is shown in Table II, the equilibrium temperatures obtained for the solfataras with native sulfur deposits are almost in agreement with the observed temperatures, although the former are always slightly higher than the latter. This implies that the native sulfur deposits occurring in solfataras are approximately in equilibrium with the solfataric gases from which the native sulfur deposit is formed, and possibly that, in the solfataric gases, the sulfur vapor is also in equilibrium with the water vapor, hydrogen sulfide and sulfur dioxide, through the reaction:

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7) O. Kubaschewski and E. I. Evans, "Metallurgical Thermochemistry," John Wiley, New York (1956).

8) F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards (1952), p. 500.

9) Y. Mizutani et al., Unpublished Data.

10) S. Sakuma, *Bull. Volcanol. Soc. Japan, 2nd Ser.*, *1*, 1 (1957).

Table I. Chemical composition of solfataric gases of volcano Nasudake

Solfatara	M-2c	OE-1	O-1	U-1
Date	1961	1962	1961	1961
Temp., °C	410	190	181	132
H_2O, l./1000 l.	993.6	991.7	982.6	991.4
CO_2, l./1000 l.	2.0	1.24	1.3	1.4
H_2S, l./1000 l.	3.08	4.23	13.7	4.10
SO_2, l./1000 l.	0.71	2.41	1.64	2.12
HCl, l./1000 l.	0.250	0.214	0.51	0.91
HF, l./1000 l.	0.041	0.056	0.14	0.01
O_2, l./1000 l.	0.000	0.000	0.000	0.000
H_2, ml./1000 l.	310	100	57	<10
N_2, ml./1000 l.	21	36	40	<86
Ar, ml./1000 l.	0.19	0.39	0.24	—
CH_4, ml./1000 l.	0.96	2.1	2.6	< 3
CO, ml./1000 l.	0.07	0.39	—	—

Table II

Solfatara	Sampling date	Native sulfur in gas channel	Mole fractions* × 10^3			H_2S/SO_2	$\frac{X^2_{H_2O}}{X^2_{H_2S}X_{SO_2}}$	Equilibrium temp. °C	Observed outlet temp. °C	Difference Eq. T.− outlet T.
			X_{H_2O}	X_{H_2S}	X_{SO_2}					
T-1	1961	+	995.4	4.2	0.49	8.6	$10^{8.06}$	161	118	+43
T-1	1962	+	997.1	2.3	0.62	3.7	$10^{8.48}$	151	119	+32
T-1	1963	+	996.3	3.6	0.11	33	$10^{8.84}$	142	120	+22
S-1	1961	+	996.6	3.2	0.16	20	$10^{8.78}$	143	120	+23
S-1	1962	+	996.7	2.6	0.72	3.6	$10^{8.31}$	154	129	+25
U-1	1961	+	993.8	4.2	2.1	2.0	$10^{7.43}$	179	132	+47
U-1	1963	+	992.7	4.8	2.5	1.9	$10^{7.23}$	185	140	+45
O-2c	1963	+	992.0	4.6	3.4	1.4	$10^{7.14}$	187	160	+27
O-1	1961	−?	984.6	13.7	1.6	8.6	$10^{6.51}$	207	181	+26
OE-1	1962	−?	993.3	4.2	2.4	1.8	$10^{7.37}$	181	190	−9
O-2	1961	−?	987.6	11.1	1.3	8.5	$10^{6.79}$	199	195	+4
M-2a	1960	−	993.7	5.9	0.36	16	$10^{7.90}$	165	195	−30
O-2b	1963	−	992.9	3.9	3.1	1.3	$10^{7.33}$	181	217	−36
O-2	1963	−	993.2	4.0	2.8	1.4	$10^{7.34}$	181	230	−49
M-2a	1961	−	997.3	5.9	0.36	2.6	$10^{8.58}$	146	261	−115

* $X_{H_2O}+X_{H_2S}+X_{SO_2}=1$

$$3/n\,S_{n(gas)} + 2H_2O = 2H_2S + SO_2 \qquad (8)$$

The Behavior of Hydrogen Sulfide and Sulfur Dioxide in Solfataric Gases.—The foregoing finding facilitates the understanding of the behavior of sulfur compounds in solfataric gases. If it is assumed that ascending volcanic water vapor comes into contact with subterranean native sulfur deposits for a sufficient time to react with them, the following reactions may be expected between water vapor and native sulfur:

$$3S_{(s,l)} + 2H_2O = 2H_2S + SO_2 \qquad (9)$$

$$H_2S = H_2 + S_{(s,l)} \qquad (10)$$

Then, on the assumption that the chemical equilibrium is established in this system, the hydrogen sulfide, sulfur dioxide, and hydrogen contents of the gas phase at a given P, T condition may be estimated by solving the following simultaneous equations:

$$K_4 = \frac{X^2_{H_2O}}{X^2_{H_2S}X_{SO_2}P} \qquad (11)$$

$$K_5 = \frac{X_{H_2}}{X_{H_2S}} \qquad (12)$$

$$\frac{2(X_{H_2S}+X_{H_2}+X_{H_2O})}{2X_{SO_2}+X_{H_2O}} = 2$$

$$= \text{Ratio of hydrogen to oxygen atoms} \qquad (13)$$

$$X_{H_2O} + X_{H_2S} + X_{SO2} + X_{H_2} = 1 \qquad (14)$$

where K_4 and K_5 are the equilibrium constants of reactions 9 and 10 respectively, P is the total pressure on the system, and X is the mole fraction of the gaseous components in the system. For the value of K_4, Eqs. 5, 6 and 7 are used again, and the value of K_5 is calculated from the standard thermodynamic properties of the chemical components in the way described above. The equation of K_5 obtained is:

$$\log K_5 = -9.475 + 2.470 \log T + 0.343 \times 10^{-3}\, T - 770\, T^{-1} + 1.313 \times 10^{3}\, T^{-2} \qquad (15)$$

The equilibrium amounts of hydrogen sulfide, sulfur dioxide, and hydrogen in the gas phase, as calculated from the simultaneous equations, are illustrated graphically in Fig. 2.

The equilibrium figure obtained shows that the H_2S/SO_2 ratio of the gas phase is always approximately 2.0, while the hydrgoen sulfide, sulfur dioxide, and hydrogen contents in the gas phase vary with the change in the P, T condition, because the hydrogen content is always so small as to be negligible as compared with the hydrogen sulfide and sulfur dioxide contents.

In the Nasudake Volcano, some solfataric gases of the low-temperature type show a H_2S/SO_2 ratio close to 2 and a paucity of hydrogen (in Table I, OE-1 and U-1). This probably implies that the major part of the sulfur compounds in the gases is derived from native sulfur deposits through the above reactions. The addition of sulfur compounds of this sort may also occur in low-temperature solfataras other than OE-1 and U-1. The situation must, however, be somewhat different from that considered for OE-1 and U-1, because the H_2S/SO_2, ratio of the gases from those solfataras is far different from 2. The gases coming from such solfataras may be considered to be products of reactions between native sulfur deposits and volcanic gases containing appreciable amounts of hydrogen sulfide, sulfur dioxide, and hydrogen. When such reactions proceed and reach an equilibrium in the gases, the equilibrium ratio, H_2S/SO_2, should deviate from 2 because the mass balance, the H/O atomic ratio in the system, is different from 2; Fig. 3 shows the effect of adding extra chemical components to the water vapor in the S-H_2O system. In other words, the equilibrium amounts of hydrogen sulfide and sulfur dioxide in the final products of the reactions at a given P, T condition are varied by the change in the amounts of such extra chemical components as hydrogen sulfide, sulfur dioxide, and hydrogen in the gases.

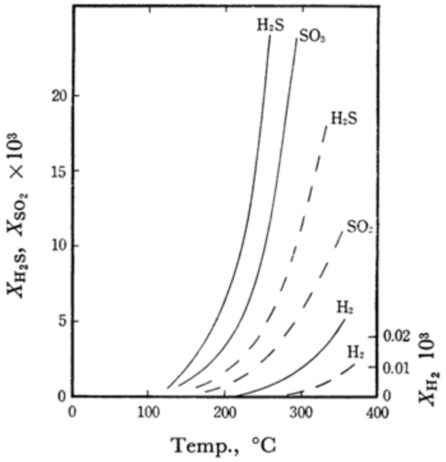

Fig. 2. Equilibrium amounts of H_2S, SO_2 and H_2 for system $S_{(lipuid)}$-$H_2O_{(vapor)}$.
Solid line: $P_{H_2O}+P_{H_2S}+P_{SO_2}+P_{H_2}=1$ atm.
Broken line: $P_{H_2O}+P_{H_2S}+P_{SO_2}+P_{H_2}=100$ atm.

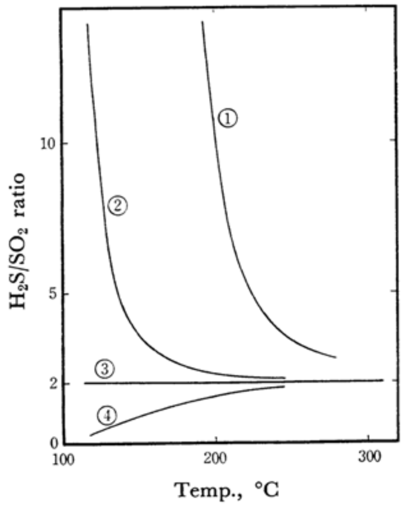

Fig. 3. Equilibrium ratio of H_2S to SO_2 for system S - H_2O - extra H_2S, SO_2 or H_2.
$P=1$ atm.
①: H/O=2.020 (H_2O : extra H_2S or H_2=990 : 10)
②: H/O=2.002 (H_2O : extra H_2S or H_2=999 : 1)
③: H/O=2.000
④: H/O=1.996 (H_2O : extra SO_2=999 : 1)

The natural situation in most low-temperature solfataras may be more complicated than this simple model indicates, but the general features of the variation in hydrogen sulfide and sulfur dioxide contents in the gases ought to be accounted for by this model if the above reactions reach equilibrium in the solfataras.

The authors wish to express their deep appreciation to Professor Shinya Oana of Nagoya University and Dr. Sadao Matsuo of Tokyo Kyoiku University for their helpful suggestions and for their encouragement throughout this work.