

The Formation of Sulfate in Water Droplets¹

W. D. SCOTT AND P. V. HOBBS

University of Washington, Seattle

(Manuscript received 20 June 1966)

ABSTRACT

Previous theoretical studies of the formation of sulfate in the SO_2 - NH_3 -liquid H_2O system have not considered in a rigorous manner the chemical equilibrium equations, and have failed to provide a satisfactory explanation for the catalytic action of the ammonia. In the present paper the equilibria involved are derived. By assuming that the limiting mechanism in the rate of production of sulfate is the oxidation of the sulfite ion, the observed catalysis of the oxidation by ammonia is explained. The theory also predicts a rate of production of sulfate which is in qualitative agreement with experimental results.

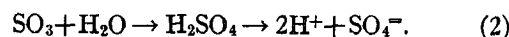
1. Introduction

Sulfate is an important constituent of rain water and aerosol particles. Its formation in the troposphere is thought to occur primarily by the oxidation of SO_2 to SO_4^{2-} . Since the sulfate is normally found in conjunction with ammonia, it is generally supposed that it exists in the form of ammonium sulfate. The evaporation of cloud and fog droplets could then lead to the formation of ammonium sulfate particles, and this would explain the fact that in industrially polluted air the large ($0.1 \mu < r < 1 \mu$) nuclei consist mainly of ammonium sulfate (Junge, 1953). The high concentration of large particles which exist in the stratosphere could result from either the upward transfer and coagulation of ammonium sulfate from the troposphere, or the oxidation of SO_2 or H_2S *in situ* (Junge, 1963).

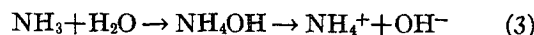
The chemical processes involved in the oxidation of SO_2 in water are not well understood. Junge and Ryan (1958) found that the oxidation of SO_2 to SO_4^{2-} in water can only take place in the presence of a catalyst and that minute traces of metal ions will serve in this capacity. However, the amount of SO_4^{2-} produced by this mechanism appears insufficient to explain the observed concentrations of SO_4^{2-} in rain water. A much more efficient conversion of SO_2 to SO_4^{2-} results if traces of NH_3 are present, and Junge and Ryan (1958) have shown that it is possible to explain the essential features of the formations of sulfate in the Earth's atmosphere by the reaction of SO_2 and NH_3 in cloud and fog droplets. Work by Cadle and Robbins (1960) has shown also that the reaction between droplets of dilute H_2SO_4 and ammonia proceeds extremely rapidly. In more recent work, Van den Heuval and Mason (1963) have measured the rate of formation of ammonium sulfate in water drops which were exposed to air

containing gaseous SO_2 and NH_3 . Although the concentrations of SO_2 and NH_3 in these experiments were much larger than those found in the Earth's atmosphere, extrapolation of the results to lower concentrations indicated that the large ammonium sulfate nuclei found in industrially polluted air could be formed through the absorption of SO_2 and NH_3 in cloud and fog droplets.

The exact nature of the catalytic action of NH_3 in the SO_2 - NH_3 -liquid H_2O system has not been explained satisfactorily in previous work. Van den Heuval and Mason suggested that the rate-limiting process in the formation of ammonium sulfate is the oxidation of SO_2 to SO_4^{2-} in oxygenated water, i.e.,



The ammonia reaction



was then considered to act as a catalyst by releasing OH^- ions to neutralize the H^+ ions. This explanation is obviously incorrect, however, since H_2SO_4 ionizes very readily, and at the concentrations at which it is present in cloud droplets all the sulfate in (2) would be present regardless of the concentration of NH_3 .

The purpose of this paper is to consider more carefully the nature of the SO_2 - NH_3 -liquid H_2O system in order to gain insight into the catalytic action of NH_3 in the formation of SO_4^{2-} .

2. The SO_2 - NH_3 -liquid H_2O system

The chemical equilibrium equations (4)-(12) for the SO_2 - NH_3 -liquid H_2O system, including carbon dioxide equilibria, are listed in Table 1. Only one non-ionized aqueous form of each gas is considered since

¹ Contribution No. 125, Department of Atmospheric Sciences, University of Washington, Seattle.

TABLE 1. Chemical equilibrium equations, equilibrium constant expression and values of equilibrium constants (25C) for SO₂-NH₃-liquid H₂O system including CO₂ equilibria.

Equation	Chemical equilibrium equation	Equilibrium constant expression	Value of the equilibrium constant at 25C
(4)	H ₂ O ⇌ H ⁺ + OH ⁻	$K_w = [H^+][OH^-]$	1.008 × 10 ⁻¹⁴ (Robinson and Stokes, 1959)
(5)	(SO ₂) _g + H ₂ O ⇌ SO ₂ · H ₂ O	$K_{hs} = [SO_2 \cdot H_2O] / P_{SO_2}$	1.24 (Johnstone and Leppla, 1934)
(6)	SO ₂ · H ₂ O ⇌ H ⁺ + HSO ₃ ⁻	$K_{1s} = [H^+][HSO_3^-] / [SO_2 \cdot H_2O]$	0.0127 (Yui, 1940; Wang and Himmelblau, 1964)
(7)	HSO ₃ ⁻ ⇌ H ⁺ + SO ₃ ⁼	$K_{2s} = [H^+][SO_3^{=}] / [HSO_3^-]$	6.24 × 10 ⁻⁸ (Yui, 1940)
(8)	(NH ₃) _g + H ₂ O ⇌ NH ₃ · H ₂ O	$K_{ha} = [NH_3 \cdot H_2O] / P_{NH_3}$	57 (Morgan and Maass, 1931)
(9)	NH ₃ · H ₂ O ⇌ NH ₄ ⁺ + OH ⁻	$K_{1a} = [NH_4^+][OH^-] / [NH_3 \cdot H_2O]$	1.774 × 10 ⁻⁵ (Robinson and Stokes, 1959)
(10)	(CO ₂) _g + H ₂ O ⇌ CO ₂ · H ₂ O	$K_{hc} = [CO_2 \cdot H_2O] / P_{CO_2}$	0.034 (Morgan and Maass, 1931)
(11)	CO ₂ · H ₂ O ⇌ H ⁺ + HCO ₃ ⁻	$K_{1c} = [H^+][HCO_3^-] / [CO_2 \cdot H_2O]$	4.45 × 10 ⁻⁷ (Robinson and Stokes, 1959)
(12)	HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ⁼	$K_{2c} = [H^+][CO_3^{=}] / [HCO_3^-]$	4.68 × 10 ⁻¹¹ (Robinson and Stokes, 1959)

there is no evidence that H₂SO₃ or NH₄OH exist in aqueous solution. Also listed in Table 1 are the appropriate expressions for the equilibrium constants and the best value for each constant.

Now the rate-limiting process in the formation of SO₄⁼ is probably an oxidation involving the SO₃⁼ ion. If SO₄⁼ is produced by a reaction between SO₃⁼ and sufficient oxygen, the rate of production of SO₄⁼ is given approximately by the first-order rate equation

$$\frac{d[SO_4^{=}]}{dt} = K[SO_3^{=}] \tag{13}$$

Manipulation of (4) to (12) allows the molar concentration of each component to be expressed in terms of a vapor pressure and the hydrogen ion concentration. In particular, the molar concentration of SO₃⁼ can be written as

$$[SO_3^{=}] = K_{2s} K_{1s} K_{hs} \frac{P_{SO_2}}{[H^+]^2} = 9.84 \times 10^{-10} \frac{P_{SO_2}}{[H^+]^2} \tag{14}$$

where P_{SO₂} is the partial pressure of the SO₂. From the electroneutrality equation we have the additional relationship

$$[H^+] + [NH_4^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{=}] + [HCO_3^-] + 2[SO_4^{=}] \tag{15}$$

Substitution of the expressions for the ionic concentrations into (15) gives

$$\{1 + 10^{11} P_{NH_3}\} [H^+] = \{0.0158 [H^+] + 1.96 \times 10^{-9}\} \times \frac{P_{SO_2}}{[H^+]^2} + \frac{3.10 \times 10^{-12}}{[H^+]} + 2[SO_4^{=}] \tag{16}$$

The average carbon dioxide concentration in the gas phase has been taken as 311 ppm in (16), and the CO₃⁼ term has been omitted since it is completely negligible over the present range of interest.

3. Comparison of theory with experimental results

The general solution of the theoretical problem is as follows. The droplet starts with zero concentration of SO₄⁼ at zero time. The initial concentration of the hydrogen ions is then the implicit solution of (16) with [SO₄⁼] equated to zero. The initial rate of production of SO₄⁼ is given by (13) and (14), and the initial rate allows the concentration of sulfate after a small interval of time to be determined. This concentration of SO₄⁼ may then be substituted into (16) and the entire procedure repeated to obtain the concentration of SO₄⁼ at some later time. As the concentration of SO₄⁼ increases the hydrogen ions increase in number. It can be seen from (14) that this will cause the concentration of SO₃⁼ to decrease and, therefore, the rate of production of SO₄⁼ should decrease. This means that the concentration of SO₄⁼ will approach a limiting value as the reaction proceeds. This negative self-catalytic behavior is in agreement with the measurements of Junge and Ryan (1958).

Values for the initial oxidation rates may be obtained without knowledge of the value of the rate constant K. The initial rate of production of SO₄⁼ is proportional to the initial concentration of SO₃⁼, and this may be calculated as a function of the concentration of SO₂ and NH₃ from (14) and (16). The first line of Table 2 shows the initial values of the pH and the concentration of sulfite corresponding to partial pressures of SO₂

TABLE 2. Initial values of the pH and the concentration of sulfite (SO₃⁼) ion for various partial pressures of SO₂ and NH₃. See text for discussion

Partial pressure of SO ₂ (atm)	Partial pressure of NH ₃ (atm)	Initial pH	Initial concentration of SO ₃ ⁼ (moles liter ⁻¹)
7 × 10 ⁻⁹	7 × 10 ⁻⁹	6.34	3.4 × 10 ⁻⁵
7 × 10 ⁻⁹	0	4.97	6.0 × 10 ⁻⁸
1.4 × 10 ⁻⁸	7 × 10 ⁻⁹	6.21	3.6 × 10 ⁻⁵
7 × 10 ⁻⁹	1.4 × 10 ⁻⁸	6.48	6.2 × 10 ⁻⁵
5 × 10 ⁻⁶	5 × 10 ⁻⁶	6.35	2.4 × 10 ⁻²
5 × 10 ⁻⁶	0	3.55	6.2 × 10 ⁻⁸

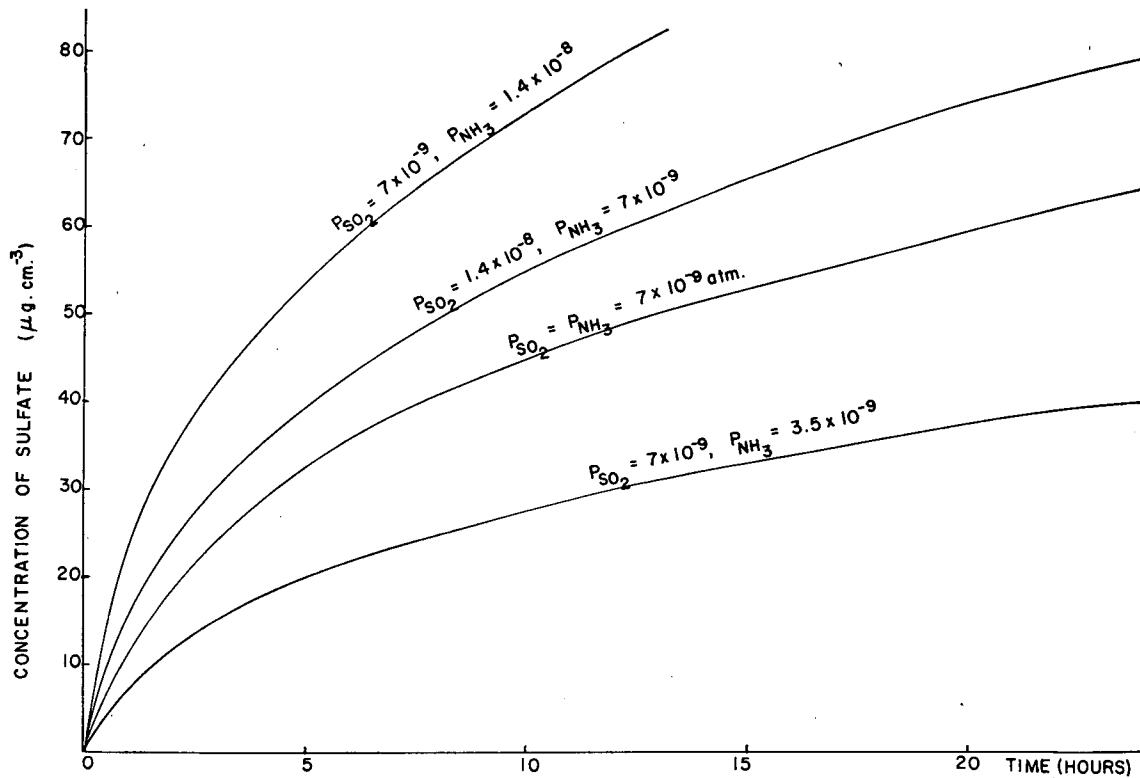


FIG. 1. Theoretical results for the concentration of sulfate in water drops as a function of time.

and NH_3 which are typical of those found in the Earth's atmosphere, namely, $20 \mu\text{gm m}^{-3}$ (7×10^{-9} atm) and $5 \mu\text{gm m}^{-3}$ (7×10^{-9} atm), respectively. The values given in the next three lines of Table 2 show the effect of varying the concentration of SO_2 and NH_3 . In the last two lines the concentrations of SO_2 and NH_3 which are taken correspond approximately to the higher concentrations used by Van den Heuval and Mason (1963).

It can be seen from the first two lines of Table 2 that the initial concentration of SO_3^- is 500 times greater when ammonia is present in concentrations similar to those found in the atmosphere than when ammonia is completely absent. Hence, under the assumed rate-limiting mechanism, the initial rate of production of SO_4^- will also be increased 500 times in the presence of ammonia. Although this result suggests that ammonia is catalyzing the reaction, it is necessary to see whether the theory predicts that the presence of ammonia will increase the amount of sulfate produced by the reaction after it has run for some time. It is to this problem that we now turn.

To determine the concentration of sulfate as a function of time the value of the rate constant K in (13) must be known. A value for K may be estimated from the experimental results of Van den Heuval and Mason since a metal ion catalyst was not present in their experiments. From the data of these workers

the value of K is found to be approximately 0.1 min^{-1} . With this value of K , and using Eqs. (13), (14) and (16), the curves shown in Fig. 1 were obtained with the aid of an IBM 7094 computer. Not shown on Fig. 1 is the case when NH_3 is absent from the system. In this case, however, the calculations show that when the partial pressure of SO_2 is equal to 7×10^{-9} atm, the concentration of sulfate after 24 hr is only $0.5 \mu\text{gm cm}^{-3}$. Hence, the theory predicts that when NH_3 and SO_2 are present in water droplets in concentrations similar to those equal in the atmosphere, the concentration of sulfate produced after 24 hr is about two orders of magnitude greater than the concentration that would be produced in the absence of NH_3 .

Junge and Ryan (1958) found in their experiments that the concentration of sulfate in water reached a limiting value after about five hours. They observed also a direct proportionality between the limiting value of the sulfate concentration and the partial pressure of the SO_2 in the environment. Although the general shapes of the theoretical curves shown in Fig. 1 are similar to the experimental curves of Junge and Ryan, the present theory does not show the concentration of sulfate reaching a limiting value even after 24 hr. Neither does the theory predict a direct proportionality between the concentration of sulfate and the partial pressure of the SO_2 . These discrepancies may result from the fact that in the experiments of Junge

and Ryan, FeCl_2 was used as a catalyst. Nevertheless, it is clear from the results that have been presented that the present theory does provide a satisfactory explanation for the catalytic action of NH_3 in the formation of sulfate in the SO_2 - NH_3 -liquid H_2O system, and it also predicts in a qualitative way the correct rate dependence for the production of the sulfate.

Acknowledgments. This research was supported by the Atmospheric Sciences Section, National Science Foundation, NSF GP-3809.

REFERENCES

- Cadle, R. D., and R. C. Robbins, 1960: Kinetics of atmospheric chemical reactions involving aerosols. *Discussions Faraday Soc.*, **30**, 155-161.
- Johnstone, H. F., and P. W. Leppla, 1934: The solubility of sulfur dioxide at low partial pressures. *J. Amer. Chem. Soc.*, **56**, 2233-2238.
- Junge, C., 1953: Die Rolle der Aerosole und der gasförmigen Beimengungen der Luft im Spurenstoffhaushalt der Troposphäre. *Tellus*, **5**, 1-26.
- , 1963: *Air Chemistry and Radioactivity*. New York and London, Academic Press, 382 pp.
- , and T. G. Ryan, 1958: Study of the SO_2 oxidation in solution and its role in atmospheric chemistry. *Quart. J. R. Meteor. Soc.*, **84**, 46-55.
- Morgan, O. M., and O. Maass, 1931: Investigations of the equilibria existing in gas water systems forming electrolytes. *Can. J. Res.*, **5**, 162-199.
- Robinson, R. A., and R. H. Stokes, 1959: *Electrolytic Solutions*. London, Butterworths, 559 pp.
- Van den Heuvel, A. P., and B. J. Mason, 1963: The formation of ammonium sulfate in water droplets exposed to gaseous sulphur dioxide and ammonia. *Quart. J. R. Meteor. Soc.*, **89**, 271-275.
- Wang, J. C., and D. M. Himmelblau, 1964: A kinetic study of sulfur dioxide in aqueous solution with radioactive tracers. *Amer. Inst. Chem. Eng. J.*, **10**, 574-579.
- Yui, T., 1940: On the electrolytic dissociation constant of sulfurous acid. *Tokyo Inst. Phys. Chem. Res. Bull.*, **19**, 1229-1236.