# Two Solid Compounds Which Decompose into a Common Vapor. Anhydrous Reactions of Ammonia and Sulfur Dioxide[1]

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**Abstract:** Measurements of vapor pressure over products of direct gaseous reactions between $NH_3$ and $SO_2$ are in agreement with a thermodynamic model which assumes the products to be two mutually soluble solids with $NH_3$:$SO_2$ stoichiometric ratios of 1:1 and 2:1. A family of curves results on a semilogarithmic plot of pressure *vs.* reciprocal temperature which forms a sloping trough when composition is added as a third dimension. The fitting procedure yields a value for the composition of each experimental solid as well as the standard enthalpies and entropies of decomposition.

Anhydrous reactions between $NH_3$ and $SO_2$ produce a complex system containing compounds in the solid state in equilibrium with a vapor phase consisting of the two gases, $NH_3$ and $SO_2$. In our laboratory[2] equilibrium vapor pressures above the solids have been measured and it appears that the system is analogous to the $NH_3$–$CO_2$ reacting system that produces ammonium carbamate.[3] Simplicity is lost, however, because more than one chemical compound is formed in the $NH_3$–$SO_2$ system. Indeed, $NH_3$ and $SO_2$ appear to have a great affinity for each other and react in nearly all stoichiometric ratios, producing red, orange, yellow, pink, and white reaction products.

Reactions between these two gases have been known for over a century and a half but they are not mentioned in most textbooks. The chemist is led to believe that $NH_3$ and $SO_2$ do not react unless they are dissolved in water and undergo a normal, weak base–weak acid neutralization reaction. Exactly which products are formed is not agreed upon. Ogawa and Aoyama[4] and Badar-ud-Din and Aslam[5] have carried out thorough analyses of the gaseous reactions. Both these investigations, as well as the experimental evidence of others,[6] support the hypothesis that a yellowish compound with an $NH_3$–$SO_2$ stoichiometric ratio of 1:1 and a white compound with a 2:1 ratio are the two primary reactions products, provided the temperature of reaction is maintained below about 10° and water is excluded from the system.

In addition, infrared absorption spectra of the vapor made in our laboratory[2] indicate that the solids decompose reversibly into $NH_3$ and $SO_2$ in the vapor, suggesting that the system is, indeed, one in which one solid phase containing two chemical compounds is in equilibrium with a common vapor of two gases, $NH_3$ and $SO_2$. This paper presents a theoretical treatment of this unusual system and compares the results with experimental data.

**Equilibrium Expressions.** Assuming that only the 1:1 and 2:1 compounds are formed, the chemical equations for their decomposition are[7]

$$NH_3 \cdot SO_2 \rightleftharpoons NH_3 + SO_2 \tag{1}$$

$$(NH_3)_2 \cdot SO_2 \rightleftharpoons 2NH_3 + SO_2 \tag{2}$$

If, furthermore, it is assumed that the two compounds form an ideal solid solution which has a mole fraction $X$ of the 1:1 compound, the following ideal equilibrium expressions are obtained

$$K_1 = \frac{P_a P_s}{X} = \frac{y(1-y)P^2}{X} \tag{3}$$

$$K_2 = \frac{P_a{}^2 P_s}{1-X} = \frac{y^2(1-y)P^3}{1-X} \tag{4}$$

where the subscripts a and s refer to the gases, ammonia and sulfur dioxide, and $y$ is the mole fraction of ammonia in the vapor. These equations can be combined to give an expression for the equilibrium total pressure $P$

$$P = \frac{X^2K_1{}^2}{(1-X)K_2} + \frac{(1-X)K_2}{XK_1} \tag{5}$$

Further, the equilibrium constants can be written in terms of the standard Gibbs free energies of decomposition, $\Delta G°$

$$\Delta G_1° = -RT \ln K_1$$

$$\Delta G_2° = -RT \ln K_2$$

Or, in terms of the standard entropy and enthalpy of reaction, the equilibrium constants are

$$K_1 = \exp\left(-\frac{\Delta G_1°}{RT}\right) = \exp\left(\frac{\Delta S_1°}{R}\right)\exp\left(-\frac{\Delta H_1°}{RT}\right)$$

$$K_2 = \exp\left(-\frac{\Delta G_2°}{RT}\right) = \exp\left(\frac{\Delta S_2°}{R}\right)\exp\left(-\frac{\Delta H_2°}{RT}\right)$$

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(1) Research supported by the Atmospheric Sciences Section of the National Science Foundation (Grant No. NSF GA-780).

(2) W. D. Scott, D. Lamb, and D. Duffy, *J. Atmos. Sci.*, **26**, 727 (1969).

(3) M. J. Joncich, B. H. Solka, and J. E. Bower, *J. Chem. Educ.*, **44**, 598 (1967).

(4) M. Ogawa and S. Aoyama, *Sci. Rept. Tohoku Univ., First Ser.*, [II] 121 (1913).

(5) Badar-ud-Din and M. Aslam, *Pakistan J. Sci. Res.*, **5**, 6 (1953).

(6) A summary of previous work is presented in another paper (see ref 2).

(7) These products have been unsystematically called amidosulfurous acid and ammonium amidosulfite or monosulfinic acid and ammonium amine monosulfinate, respectively. Since the true structure of the compounds is not well known, it is appropriate at present to use the simple stoichiometric formulas.

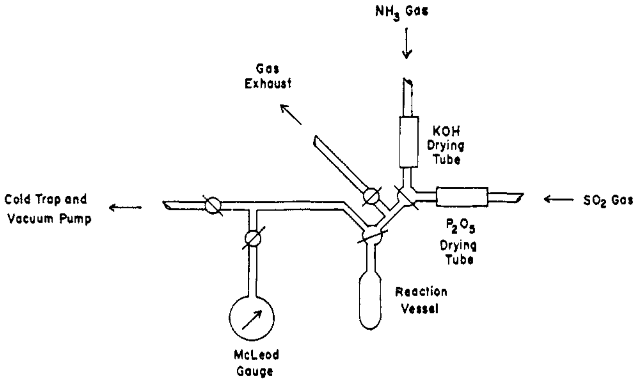


Figure 1. Vapor pressure apparatus and reaction vessel.

The temperature dependence of the equilibrium total pressure is, therefore

$$P = \frac{X^2}{1 - X} A \exp\left(\frac{\alpha}{T}\right) + \frac{1 - X}{X} B \exp\left(\frac{\beta}{T}\right) \quad (6)$$

where

$$A = \exp\left(\frac{2\Delta S_1^\circ - \Delta S_2^\circ}{R}\right) \quad B = \exp\left(\frac{\Delta S_2^\circ - \Delta S_1^\circ}{R}\right)$$

$$\alpha = \frac{\Delta H_2^\circ - 2\Delta H_1^\circ}{R} \quad \beta = \frac{\Delta H_1^\circ - \Delta H_2^\circ}{R} \quad (7)$$

As a result of the relative importance of the two terms on the right side of eq 6, a plot of log $P$ *vs.* $1/T$ at constant $X$ produces curves with two distinct slopes at the extremes of temperature. Measurements of the two slopes directly establish values of $\alpha$ and $\beta$ (or $\Delta H_1^\circ$ and $\Delta H_2^\circ$). Best values of $A$ and $B$ (or $\Delta S_1^\circ$ and $\Delta S_2^\circ$) are obtained by trial and error. Later, it will be shown that with a family of curves of constant $X$ values, it is possible to obtain best $X$ values as well as the standard enthalpies and entropies.

## Experimental Section

Experimental details are presented in our previous paper.[2] A diagram of the glass experimental apparatus is shown in Figure 1. Both gases were frozen onto the inner walls of a reaction vessel with a liquid nitrogen bath. The vessel was then allowed to warm and the gases reacted violently at about −10°. The steady-state pressures at temperatures between −10 and −70° were then measured using a McLeod gauge; the data are presented as points in Figure 2.

The apparatus had two potentially limiting features. First, the McLeod gauge is limited in use to substances which do not condense out in the compression section of the gauge. No effects of condensation in the gauge were noted, however. Second, the system exposed the sample to relatively large surfaces of glass, stopcock grease, and mercury, and thus to probable sorption. Consequently, large equilibration times were required and hysteresis effects were observed. As a result a pressure measurement over a given product generally was reproducible to only about 30%. Furthermore, data in the lowest decade shown are limited by the readability of the McLeod gauge, the precision of which was 0.002 Torr.

## Fitting the Data

The products of the reaction coated the walls of the reaction vessel and contained at least ten times the material in the vapor. Therefore, it is a good approximation to consider that the mass of the solid was not appreciably altered by sublimation into the vapor during the pressure measurements at selected temperatures. The mole fraction of 1:1 compound, $X$, can therefore be assumed constant during the measurements of pressure over a given sample.

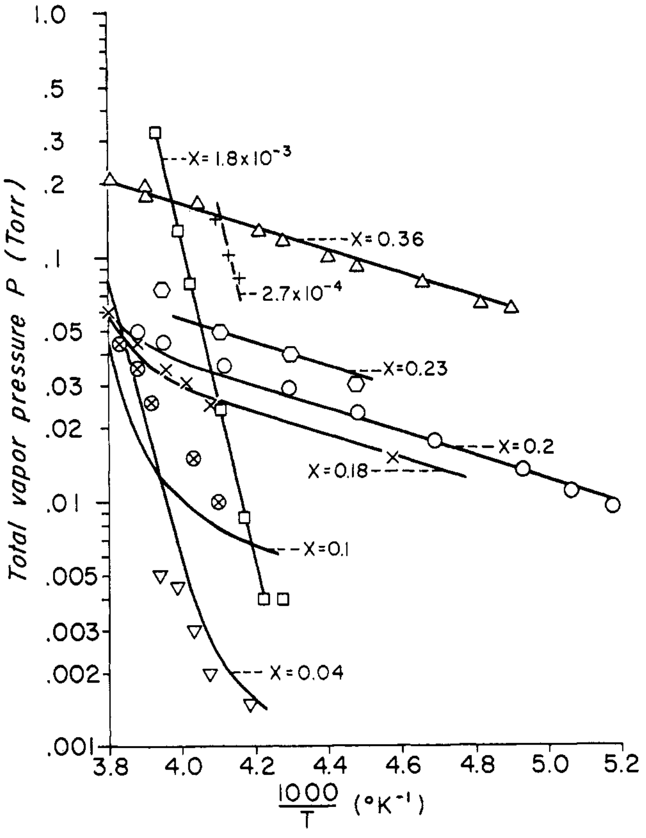


Figure 2. Experimental vapor pressure measurements (symbols) with theoretical curves superimposed.

The theoretical expression (eq 6) can be used to interpret the data in Figure 2. The final theoretical curves are drawn upon the graph. Two straight lines do, indeed, naturally occur in the data. The requirement that all parameters of the model be physically meaningful necessitates that the absolute value of $\alpha$ be less than that of $\beta$. This requires that the 1:1 compound predominates where the slope is smallest. The values of $\alpha$ and $\beta$ that give a best fit are −1080 and −15,100°K, respectively.

Using these values, the exponential terms in eq 6 are determined for all temperatures. Corresponding to each set $i$ of data at constant $X$ there is a pair of preexponential factors $M_i$ and $N_i$ that form a best fit to the data

$$M_i = \frac{X_i^2}{1 - X_i} A \quad N_i = \frac{1 - X_i}{X_i} B \quad (8)$$

By eliminating the $X_i$ in eq 8 an expression relating to $A$ to $B$ can be obtained

$$A = \frac{M_i N_i (N_i + B)}{B^2} \quad (9)$$

This expression is valid for all curves, so that for any two sets ($i$ and $j$) of data

$$B = \frac{M_j N_j^2 - M_i N_i^2}{M_i N_i - M_j N_j} \quad (10)$$

Back-substitution into eq 9 then gives a corresponding value of $A$. The constants $A$ and $B$ were calculated

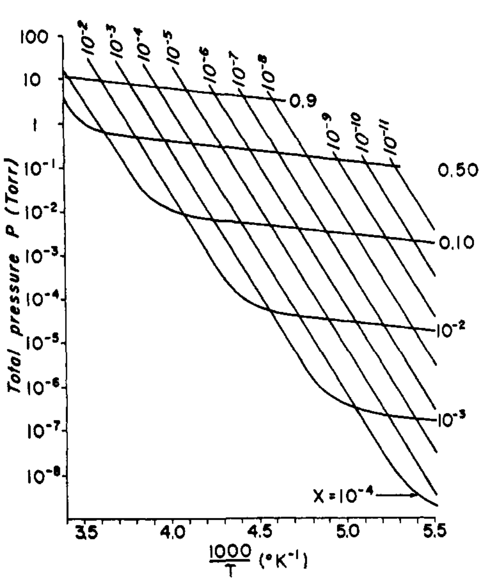


Figure 3. Calculated total vapor pressures above solid mixtures containing a constant mole fraction $X$ of the 1:1 compound.

for all possible sets of curves; the best value was selected for a best fit of the data. The values obtained were $A = 56$ Torr and $B = 3.7 \times 10^{22}$ Torr. Substituting the values for $A$, $B$, $\alpha$, and $\beta$ into eq 7, standard entropies and enthalpies of decomposition of the pure compounds can be calculated. The values refer to the decomposition of the pure solids into the gases, $NH_3$ and $SO_2$, at atmospheric pressure and are listed in Table I. Values of $X$, the mole fraction of 1:1 compound in the solid, are then calculated using eq 8. These $X$ values are shown in Figure 2 along with the theoretical curves for the above values of $A$, $B$, $\alpha$, and $\beta$.

**Table I.** Standard Enthalpies and Entropies of Decomposition of the Compounds

| Compound | $\Delta H°$, kcal/mol | $\Delta S°$, cal/(mol °K) |
|---|---|---|
| $NH_3 \cdot SO_2$ | 32.2 | 84.8 |
| $(NH_3)_2 \cdot SO_2$ | 62.2 | 174.8 |

The theoretical curves fit the data within the experimental accuracy. The significant point, of course, is that the data are well described by the interaction of two straight lines.

## Discussion

To show their behavior in the extremes of pressure and composition, the theoretical curves for constant $X$ are replotted on a larger scale in Figure 3. The curves show several interesting features. Visualizing the curves in space, with composition as a third dimension, they form a trough that slopes toward lower temperatures (higher values of $1000/T$) and smaller values of $X$. When there is a large excess of $NH_3$ in the vapor (large $y$) the steep, constant $X$ curves in the "background" (lines of small $X$) apply and the 2:1 compound predominates in the solid mixture. Increasing the amount of $SO_2$ in the vapor then results in a general lowering of the vapor pressure curves due to the formation of the 1:1 compound in solid solution. Eventually, however, the contribution of the 1:1 compound to the total vapor pressure becomes comparable to that of the 2:1 compound. At this point the $X$ lines become curved (develop "knees") and fold into the "foreground" (lines with $X \sim 1$) surface of lines with a lesser slope. As the amount of $SO_2$ is further increased ($y$ decreases), the $X$ lines move upward and the amount of 2:1 compound in the solid becomes negligibly small. However, even at this point, this small amount of 2:1 compound has a marked effect on the total vapor pressure. It is also significant that neither compound can exist in a pure form. The pure state of either solid is most nearly approached when there is an extremely large excess of one of the gases in the vapor.

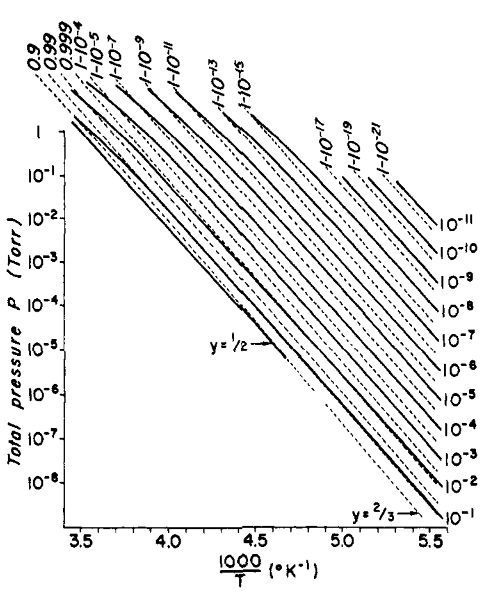


Figure 4. Calculated total vapor pressures above solid mixtures in equilibrium with a vapor containing a constant mole fraction $y$ of $NH_3$.

The "knees" of the curves are noteworthy in their relationship to the standard techniques for the measurement of equilibrium partial pressures. They define a minimum critical vapor pressure, $P_c$, exerted by any of the solid mixtures at a given temperature. Corresponding to this $P_c$ there exists a critical mole fraction of 1:1 compound, $X_c$. This $X_c$ is found by differentiating the equation for the total pressure (eq 6) with respect to $X$ and setting the derivative equal to zero. The resulting expression is

$$\frac{(1 - X_c)^2}{X_c^3(2 - X_c)} = \frac{A}{B} \exp\frac{(\alpha - \beta)}{T} = \frac{K_1^3}{K_2^2} \tag{11}$$

This equation and eq 6 determine the line $P_c = P_c(T)$ which is the locus of the "knees" of the curves.

The rather complex form of eq 11 does not show the simple stoichiometric ratios that exist in the vapors over these solid solutions. Consider curves of constant $y$, the mole fraction of ammonia in the vapor. The equations of these curves are found by solving eq 3 for $X$ and substituting into eq 4. An implicit equation containing $y$ and $P$ results

$$\frac{1}{y(1 - y)} = \frac{P^2}{K_1} + \frac{yP^3}{K_2} \tag{12}$$

These curves of constant $y$ are plotted on Figure 4. They are nearly straight lines, with a small negative curvature at higher temperatures. In the surface of $y$ lines it appears that the $y$ lines are nearly parallel and the "knee" curve is one of constant $y$. This is true only at the extremes of temperature. If the equilibrium constant expressions (eq 3 and 4) are substituted into the right side of eq 11, a simpler expression for the critical mole fraction of $NH_3$ in the vapor, $y_c$, is obtained

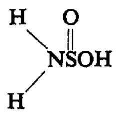
$$y_c = \frac{2 - X_c}{3 - X_c} \qquad (13)$$

This equation can also be obtained by differentiating eq 12 with respect to $y$, setting $dP/dy = 0$, and using eq 4. The extremes of this equation are interesting in light of the normal techniques for measuring the equilibrium constant in systems containing but a single compound in the solid phase. If $X_c \simeq 1$, then $y_c = 1/2$. This line is indicated by the upper arrow in Figure 4. It is exactly the line for a hypothetical, pure 1:1 solid that is not affected by another compound being present. It represents the hypothetical experiment in which the 1:1 compound exists in a pure form and its vapor pressure is simply measured. Then the sublimed vapor above the solid must be the $NH_3:SO_2$ ratio of the solid and $y = 1/2$. If $X_c \ll 1$, then $y_c = 2/3$. This is the corresponding vapor pressure curve for a hypothetical, pure 2:1 solid. The line is indicated by the lower arrow; it is nearly identical with the $y = 0.9$ curve.

Of course, real substances are not generally pure and if there is a tendency for the formation of other compounds, the stoichiometry of the solid will not be maintained in the vapor. The authors suggest that there is a slight tendency toward the formation of the 1:1 compound in the $NH_3$–$CO_2$ system, forming carbamic acid. This may explain the differences between the values of the thermodynamic properties of ammonium carbamate that have been obtained by different workers.[3]

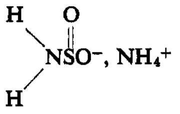
It is important not to be misled into believing that enthalpies of formation are directly associated with the slopes of the $X$ curves since this system is complex and must be considered rigorously as a whole. Generally, however, the pressure of the vapor above a solid phase that contains large amounts of the 2:1 compound exhibits the largest dependence on temperature, whereas mixtures containing mostly the 1:1 compound exhibit a relatively small dependence of pressure on temperature, so that the curves of Figure 3 cross. This means that the 2:1 compound is the more volatile at higher temperatures and the 1:1 compound is the more volatile at lower temperatures.

The compounds themselves do not vaporize but decompose reversibly into $NH_3$ and $SO_2$. The enthalpies of decomposition of the solids, in Table I, reflect heats released both in sublimation and the breaking of chemical bonds between the two gases. It is unlikely that the heat of sublimation of the 1:1 compound is greater than about 15 kcal/mol, so the additional intramolecular bonding of the 1:1 compound must account for more than about 17 kcal/mol. This energy indicates strong chemical bonding in the solid compounds which may be represented by the covalent acid structure



**1**

The 2:1 compound would then have the ionic structure

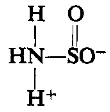


**2**

which would have high bonding energy.

However, it was observed that when two of the products were dissolved in water,[2] the solution pH was very close to 7.0. This may be explained by assuming that some portion of the product contained the acid **1** and formed acidic constituents in solution whereas another portion of the product contained the salt **2** and formed basic constituents in solution. The pH of ammonium bisulfite solutions is approximately 4.0; the pH of ammonium sulfite solutions is approximately 8.0.[8] The acidic and basic elements then merely neutralize each other.

But it is not generally expected that the portions of acid and base will exactly form a neutral solution. It is more likely that the structure **1** transforms into the tautomer, a zwitterion



$$\mathrm{H\underset{H^+}{\overset{H}{N}}{-}\overset{O}{S}O^-}$$

which tends to be a neutral buffer. The 2:1 salt would be expected to contribute very little basic strength to the solution, in any case, since the pH of ammonium sulfite solutions is approximately 8.

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[8] W. D. Scott and J. L. McCarthy, *Ind. Eng. Chem. Fund.*, **6**, 40 (1967).