

Letter to the Editor

Acid-Base Equilibria in Open Atmospheric Gas-Liquid Systems

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Abstract

Analysis of acid-base equilibria in open atmospheric gas-liquid systems was performed. Usually acid-base equilibria are considered as a function of hydrogen ion concentration as an independent variable. In this work the analysis was performed including the dependence of hydrogen ion concentration on the composition of a system. Such an approach allowed us to find the important, from the point of view of atmospheric water acidification, dependence between system composition and the liquid phase hydrogen ion concentration.

In the first stage of the work a thermodynamic model of the studied systems was formulated and then it was used to determine the effect of acidic and alkaline atmospheric gaseous pollutants on the liquid phase pH and equilibrium composition. In the final stage of the work the obtained results were generalized to any open atmospheric gas-liquid systems of the type NH_3 – strong bases – strong acids – weak acids – CO_2 – H_2O . General equations for hydrogen ion concentration and criteria for neglecting the effect of acidic gaseous pollutants were derived. These equations and criteria are an effective and easy-to-use tool for examination and interpretation of equilibria in complex open gas-liquid atmospheric systems of the type NH_3 – strong bases – strong acids – weak acids – CO_2 – H_2O .

Keywords: open atmospheric systems, acidic and alkaline atmospheric pollutants, acid-base equilibria, equilibrium composition, pH

Introduction

Limitation of the more and more spreading phenomenon of acid wet deposition encounters difficulties resulting from the extreme complexity of air chemistry and nonlinearity of chemical processes leading to acidification of atmospheric water. In spite of undertaken efforts in reduction of SO_2 and NO_x emissions (the main precursors of strong acids in the atmosphere), an adequately proportional decrease in acidity of atmospheric water has not been observed. Effective prevention of this phenomenon by using proper emission control strategies requires better understanding of the

nature of the processes leading to atmospheric water acidification.

One of the most important processes determining pH and composition of the atmospheric water is absorption of gaseous pollutants in it. Undoubtedly, knowledge of chemical equilibria in the atmospheric gas-liquid systems can help to understand this process better.

Due to the large number of species and their nature, describing the processes occurring in atmospheric systems is very difficult. These systems can be studied performing field measurements. However, the results obtained in such a way do not explain the nature of these processes enough. A convenient and flexible tool to study chemism of pollutant transformation in the atmosphere is theoretical analysis based on mathematical modelling. Mathemat-

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ical models do not need to be completely realistic in order to lead to fruitful generalization and valuable insight into the nature of the processes occurring in the considered systems. Models improve our ability to describe and measure these systems. The thermodynamic models are very useful for this purpose. They help to identify key variables describing the studied system and determine boundaries for the reacting system. Since atmospheric gas-liquid systems are often in equilibrium or close to equilibrium [1-6] the results obtained from the thermodynamic models will be more valuable.

Since the control variable in any acid-base equilibrium is pH, the equilibrium composition of the systems is usually considered a function of pH as independent variable [6 – 10]. Though such an approach allows us to learn the concentration distribution of the liquid phase species over a wide range of pH, we do not know what system of the liquid phase has this value of pH. Thus, we do not learn here an important, from the viewpoint of atmospheric water acidification, relation between system composition and liquid phase pH. Such information can be obtained by analyzing the equilibrium composition of the system as a function of pH, which in turn is a function of an assumed composition of the system. However, such a task is more difficult the more complex a system is. In the literature equations for equilibrium composition of a system, also equations for hydrogen ion concentration are given for the simplest systems only [11-13]. In the case of more complex systems the set of equations describing equilibrium of the studied system is solved by numerical methods. However, both quantity and range of such performed studies are limited and naturally there is a lack of any generalizations. These studies also do not give analytical expressions which show evidently dependency between equilibrium concentration of a given species (including hydrogen ion) and composition of the system. Expressions showing such relations would enable deeper interpretation of equilibrium states in the atmospheric water and make it easier to analyze the effect of qualitative and quantitative composition of the system on equilibrium composition and pH of the liquid phase. Such equations show directly on which components of the system equilibrium concentration of a given species depends and what kind of function it is. It cannot be seen directly from a few dozen equations, which are to be solved simultaneously.

The aim of this work was thermodynamic analysis of complex open atmospheric gas-liquid systems carried out treating hydrogen ion concentration as a variable dependent on the system composition.

In the atmosphere, open gas-liquid systems (the systems of practically constant partial pressures of gaseous components) may occur under the following conditions:

- when the stationary state between emissions and/or production of gaseous pollutants in the atmosphere and their removal from the gas phase is established
- at counter-current movement of air and raindrops

when atmospheric water is presaturated with soluble gases at higher altitudes

- when the aqueous phase is in equilibrium with an infinite volume of the gas phase (when a water-to-air volume ratio is approaching zero); low liquid-to-air volume ratios are typical of aerosols.

In the first stage of the work a thermodynamic model of the studied systems was developed and then it was used to determine the influence of individual gaseous pollutants and their mutual ratios in the gas phase on pH and equilibrium liquid phase composition. In the final stage of the work the obtained results were generalized to any open atmospheric gas-liquid systems of the type NH_3 – strong bases – strong acids – weak acids – CO_2 – H_2O .

Thermodynamic Model

Thermodynamic model of multicomponent gas – liquid system equilibrium consists of a system of equations describing phase and chemical equilibria established in the system, as well as material and charge balance equations:

$$K_{aj}^g(T, p) = \frac{a_{m_i}}{m_i^{\nu_{ij}}} = \frac{m_i \gamma_{mi}}{m_i^{\nu_{ij}}} \quad (1)$$

$$\frac{a_{p_i}}{p_i^{\nu_{ij}}} = \frac{p_i}{p_i^{\nu_{ij}}}$$

$$i = 1, \dots, k$$

$$K_{aj}^l(T, p) = \prod_i \left(\frac{a_{m_i}}{m_i} \right)^{\nu_{ij}} = \prod_i \left(\frac{m_i \gamma_{mi}}{m_i} \right)^{\nu_{ij}} \quad (2)$$

$$j = 1, \dots, R$$

$$i = 1, \dots, n$$

$$m_{TA} = \sum m_{mA} + \sum m_{iA} \quad (3)$$

$$\sum z_i m_i = 0 \quad (4)$$

where: $K_{aj}^g(T, p)$ - thermodynamic equilibrium constant for $i_{(g)} \leftrightarrow i_{(l)}$, $K_{aj}^l(T, p)$ - thermodynamic equilibrium constant for j -th reaction in the solution, k – number of species in the gas phase, n – number of species in the liquid phase, R – number of independent chemical reactions in the liquid phase, a_{p_i} - pressure activity of species i in the gas phase, a_{m_i} - molal activity of species i in the liquid phase, p_i - partial pressure of species i , m_i - molal concentration of species i , mol/kg H_2O , γ_{mi} - molal activity coefficient of species i in the liquid phase, p^\ominus , m^\ominus - pressure and concentration in standard state, respectively ($p^\ominus = 1$ bar, $m^\ominus = 1$ mol/kg H_2O), ν_{ij} - stoichiometric coefficient of species i in reaction j , m_{TA} - total concentration of species A (sum of the concentrations of ionic and molecular forms) in the solution, mol/kg H_2O , $\sum m_{mA}$ - concentration of molecular species A in the solution, mol/kg H_2O , $\sum m_{iA}$ - concentration of ionic species A in the solution, mol/kg H_2O , z_i - charge of ion i .

Under atmospheric conditions the gas may be assumed ideal and then it may be assumed that $a_{pi} = p_i$. Molal activity coefficients γ_{mi} were calculated by an equation derived from Pitzer's theory [14 – 16]:

$$\begin{aligned} \ln \gamma_{mi} = & -A_{\phi} z_i^2 \left[\frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b} \ln(1 + bI^{0.5}) \right] + \\ & 2 \sum_{j \neq i} m_j \left\{ \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_i I} \left[1 - \left(1 + \alpha_i I^{0.5} \right) \exp(-\alpha_i I^{0.5}) \right] \right\} + \\ & \frac{2\beta_{ij}^{(2)}}{\alpha_i^2 I} \left[1 - \left(1 + \alpha_i I^{0.5} \right) \exp(-\alpha_i I^{0.5}) \right] - \\ & \frac{z_i^2}{I^2} \sum_{j \neq i} \sum_{k \neq i} m_j m_k \left\{ \frac{\beta_{ijk}^{(0)}}{\alpha_i} \left[1 - \left(1 + \alpha_i I^{0.5} + 0.5\alpha_i^2 I \right) \exp(-\alpha_i I^{0.5}) \right] \right\} + \\ & \frac{\beta_{ijk}^{(2)}}{\alpha_i^2} \left[1 - \left(1 + \alpha_i I^{0.5} + 0.5\alpha_i^2 I \right) \exp(-\alpha_i I^{0.5}) \right] \end{aligned} \quad (5)$$

where A_{ϕ} is the Debye-Hückel constant, I is the ionic strength of the solution, α_i has the value 2.0 for 1-1 and 2-1 electrolytes (terms with α_2 are omitted), for 2-2 electrolytes $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$, $b = 1.2$ for all electrolytes, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ - Pitzer's ion interaction parameters, i, j, k - ion or molecular species, w - water.

The system of equations (1) – (5) was solved numerically using the Newton-Raphson method [17, 18]. Equilibria considered in the calculations are listed in Table 1.

Effect of Atmospheric Gaseous Pollutants of Major Importance on Equilibrium Composition and pH of the Liquid Phase

From among primary and secondary gaseous pollutants present in the atmosphere, gases of acidic and alkaline nature easily soluble in water were taken into consideration: NH_3 , H_2SO_4 , HNO_3 , HCl , HNO_2 , SO_2 and CO_2 . In order to determine their effect on composition and pH of the aqueous phase calculations of its equilibrium, compositions were made changing the composition of the gas phase. Concentrations of the gaseous components were chosen in such a way that conclusions correct for the full range of atmospheric concentrations of individual gases could be drawn with as small a number of calculations as possible. The following general principle was adopted: for the calculations the strong acid concentrations were assumed lower than the typical atmospheric concentrations and the weak acid concentrations were assumed to be higher. However, ammonia concentration was being changed in a wide range of concentrations from the lower to slightly higher than the atmospheric ones. Ammonia is the only common alkaline gas in the atmosphere and it plays a key role in limiting the acidity of atmospheric water droplets. Due to its alkaline nature and high solubility in water even very little changes in the NH_3 gas-phase concentration have a considerable effect on the ionic composition and pH of atmospheric water.

Table 1. Thermodynamic equilibrium constants at 298.15 K.

Equilibrium	K_a^H or K_a	References
$\text{NH}_{3(\text{g})} + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 \cdot \text{H}_2\text{O}$	55.74	[19]
$\text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$	$1.774 \cdot 10^{-5}$	[20]
$\text{H}_2\text{SO}_{4(\text{g})} \leftrightarrow \text{H}_2\text{SO}_{4(\text{aq})}$	$2.484 \cdot 10^{13}$	*
$\text{H}_2\text{SO}_{4(\text{aq})} \leftrightarrow \text{H}^+ + \text{HSO}_4^-$	1000.0	[21]
$\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}$	$1.03 \cdot 10^{-2}$	[22]
$\text{HNO}_{3(\text{g})} \leftrightarrow \text{HNO}_{3(\text{aq})}$	$1.983 \cdot 10^5$	[13]
$\text{HNO}_{3(\text{aq})} \leftrightarrow \text{H}^+ + \text{NO}_3^-$	15.4	[23]
$\text{HNO}_{2(\text{g})} \leftrightarrow \text{HNO}_{2(\text{aq})}$	49	[23]
$\text{HNO}_{2(\text{aq})} \leftrightarrow \text{H}^+ + \text{NO}_2^-$	$5.1 \cdot 10^{-4}$	[23]
$\text{HCl}_{(\text{g})} \leftrightarrow \text{HCl}_{(\text{aq})}$	1.1	[24]
$\text{HCl}_{(\text{aq})} \leftrightarrow \text{H}^+ + \text{Cl}^-$	$1.7 \cdot 10^6$	[24]
$\text{SO}_{2(\text{g})} + \text{H}_2\text{O} \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O}$	1.23	[22]
$\text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+$	$1.23 \cdot 10^{-2}$	[22]
$\text{HSO}_3^- \leftrightarrow \text{SO}_3^{2-} + \text{H}^+$	$6.6 \cdot 10^{-8}$	[22]
$\text{CO}_{2(\text{g})} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 \cdot \text{H}_2\text{O}$	$3.4 \cdot 10^{-2}$	[22]
$\text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$	$4.5 \cdot 10^{-7}$	[22]
$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	$4.7 \cdot 10^{-11}$	[22]
$\text{HCOOH}_{(\text{g})} \leftrightarrow \text{HCOOH}_{(\text{aq})}$	$3.7 \cdot 10^3$	[25]
$\text{HCOOH}_{(\text{aq})} \leftrightarrow \text{H}^+ + \text{HCOO}^-$	$1.8 \cdot 10^{-4}$	[25]
$\text{CH}_3\text{COOH}_{(\text{g})} \leftrightarrow \text{CH}_3\text{COOH}_{(\text{aq})}$	$5.0 \cdot 10^3$	[25]
$\text{CH}_3\text{COOH}_{(\text{aq})} \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^-$	$1.8 \cdot 10^{-5}$	[25]
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$1.008 \cdot 10^{-14}$	[20]

* K_a^H for H_2SO_4 has been calculated on the basis of the equilibrium constants for $\text{H}_2\text{SO}_{4(\text{g})} \leftrightarrow \text{H}^+ + \text{HSO}_4^-$ [26] and $\text{H}_2\text{SO}_{4(\text{aq})} \leftrightarrow \text{H}^+ + \text{HSO}_4^-$ [21].

Strong acids and ammonia have the greatest influence on the liquid phase equilibrium composition. Weak acids may have an impact when their concentrations are sufficiently high and strong acid concentrations are sufficiently low. If it turns out that at the assumed low concentration of the strong acid and high concentrations of weak acids the strong acid have a decisive effect on the equilibrium composition, it will be also true at higher strong acid concentrations. Thus, with such selection of concentrations, conclusions drawn on the basis of the calculation results for the extreme concentrations are correct not only for these extreme cases but also for the intermediate ones, including those which correspond to typical atmospheric concentrations.

The calculations were made for temperature 298K. The most representative results are presented in Figures 1-3. The equilibrium concentrations of each species in the solution differ so considerably that in order to put them together in the same figure so as to see changes in

the lowest concentrations, the logarithmic scale had to be used. While analyzing the diagrams we should keep in mind that the logarithmic scale visually lessens the significance of species of high concentrations and increases those of low concentrations.

Fig. 1 shows the dependence of the liquid phase equilibrium composition on NH_3 gas-phase concentration for the following concentrations of other gaseous constituents: SO_2 - 1 ppm, H_2SO_4 - $2.5 \cdot 10^{-18}$ ppm, HNO_3 - 10^{-6} ppm, HNO_2 - 10^{-4} ppm, CO_2 - 350 ppm. The NH_3 gas-phase concentration was changed over a wide (from the atmospheric point of view) range from $1 \cdot 10^{-4}$ ppm up to 0.1 ppm. At very low NH_3 gas-phase concentration ($\leq 10^{-4}$ ppm) the predominant species in the aqueous phase are NH_4^+ , H^+ , NO_3^- and SO_4^{2-} ions. As gaseous NH_3 concentration increases, hydrogen ion concentration decreases, whereas NH_4^+ , SO_4^{2-} and NO_3^- concentrations increase. SO_4^{2-} concentration increases more strongly than NO_3^- concentration. Thus, at higher gaseous NH_3 concentrations (above 10^{-3} ppm), predominant species in the solution are only NH_4^+ and SO_4^{2-} ions. Despite increasing NH_3 concentration up to a high level (for atmospheric conditions) the aqueous phase remains acidic; pH ranges from 2.90 to 4.08.

As results from the above, even at low concentrations of gaseous components of strong acidic nature they have decisive influence on the liquid phase equilibrium composition despite high SO_2 concentration. Sulphur dioxide may have an effect only when the system has no strong acids or they are present at very low concentrations. The results of calculations for such conditions are shown in Fig. 2. The SO_2 gas-phase concentration was being changed from 10^{-6} ppm to 1 ppm with the following assumed concentrations of the other gas phase components: NH_3 - 1 ppm, CO_2 - 350 ppm, HNO_2 - 10^{-6} ppm.

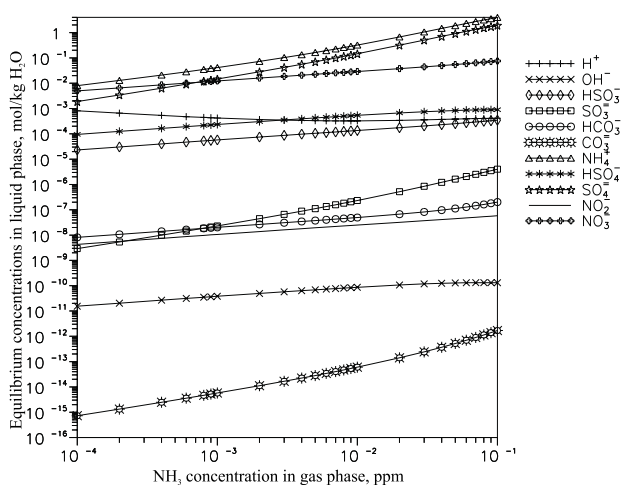


Fig. 1. Effect of NH_3 concentration in the gas phase on the equilibrium composition of the liquid phase at other gaseous species concentrations: SO_2 - 1 ppm, H_2SO_4 - $2.5 \cdot 10^{-18}$ ppm, HNO_3 - 10^{-6} ppm, HNO_2 - 10^{-4} ppm, CO_2 - 350 ppm.

If SO_2 concentration is lower than 10^{-5} ppm, NH_4^+ and HCO_3^- ions are major species in the solution and their concentrations are practically the same. Within this range, HSO_3^- and SO_3^{2-} concentrations are much lower than those of NH_4^+ and HCO_3^- . However, as gaseous SO_2 concentration increases, HSO_3^- and SO_3^{2-} concentrations also increase while HCO_3^- concentration falls. As a result, HCO_3^- , HSO_3^- and SO_3^{2-} concentrations are approximately of the same order within the range of SO_2 concentrations of 10^{-5} - 10^{-3} ppm. At still higher SO_2 concentrations (above 10^{-3} ppm) the major species in the aqueous phase besides NH_4^+ are HSO_3^- and SO_3^{2-} ions, and HCO_3^- ion concentration is not of great importance. SO_3^{2-} ion concentration is higher than HSO_3^- concentration up to the gas phase SO_2 concentration of about 10^{-2} ppm. At higher SO_2 concentrations HSO_3^- ions predominate over SO_3^{2-} ions. With SO_2 concentrations ranging from 10^{-6} to 1 ppm, the liquid phase pH changes from 8.13 to 6.30.

NO_2^- ion concentration is very low within the whole range of SO_2 concentrations. It follows that gaseous HNO_2 practically has no effect on the aqueous phase equilibrium if its concentration is lower than about 10^{-6} ppm. However, the effect of HNO_2 on H^+ ion concentration in the presence of SO_2 cannot finally be excluded at higher HNO_2 concentrations because dissociation constants for HNO_2 and SO_2 differ only about 24 times.

Fig. 3 presents the results of calculations performed with an assumption that in the gas phase are present only NH_3 at concentration of 1 ppm, CO_2 at 350 ppm and HNO_2 at varied concentrations of $1 \cdot 10^{-5}$ - $1 \cdot 10^{-2}$ ppm. At gaseous HNO_2 concentration below 10^{-5} ppm the dominant species in the liquid phase are NH_4^+ and HCO_3^- ions and their concentrations are practically equal. In this range HNO_2 does not affect the liquid phase equilibrium composition, in spite of high NH_3 concentration

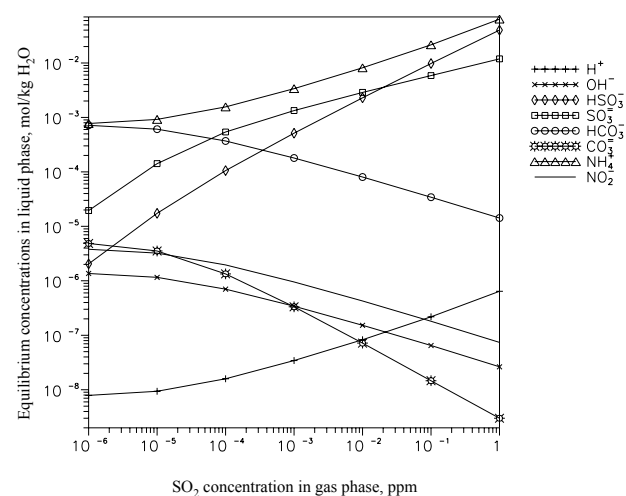


Fig. 2. Effect of SO_2 concentration in the gas phase on the equilibrium composition of the liquid phase at other gaseous species concentrations: NH_3 - 1 ppm, HNO_2 - 10^{-6} ppm, CO_2 - 350 ppm.

(1 ppm) – alkaline component, which increases HNO_2 solubility in the solution.

With the increase in $\text{HNO}_{2(g)}$ concentration above 10^{-5} ppm, HCO_3^- concentration drops and NH_4^+ concentration rises. NO_2^- ion concentration also rises and at $\text{HNO}_{2(g)}$ concentrations equal to or higher than 10^{-3} ppm NO_2^- concentration is practically the same as NH_4^+ concentration. HCO_3^- ion is not the main species any longer. It is replaced by NO_2^- ion.

Gaseous HNO_2 practically does not influence the liquid phase equilibrium composition when its concentration is equal to or lower than 10^{-5} ppm. At higher concentrations it may or may not affect the liquid phase equilibrium composition, depending on the other kind of acid gases present in the gas phase.

In order to estimate the influence of alkaline components other than NH_3 on the equilibrium composition and pH of the aqueous phase, calculations were made for the system where Ca^{2+} ions (coming, for instance, from dissolution of solid atmospheric aerosol particles) are included in the water phase. The calculations were made for three different Ca(II) ion concentrations in the liquid phase: $1 \cdot 10^{-4}$, $1 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ mol/kg and for the following gas phase composition: $\text{H}_2\text{SO}_4 - 1 \cdot 10^{-18}$ ppm, $\text{HNO}_3 - 1 \cdot 10^{-6}$ ppm, $\text{CO}_2 - 350$ ppm. NH_3 concentration in the gas phase was being changed from $1 \cdot 10^{-5}$ ppm to $2 \cdot 10^{-2}$ ppm. It should be emphasized that the solubility products for calcium compounds have not been exceeded for any of the analyzed cases. The results are presented in Fig. 4. For comparison, the results for zero Ca(II) content also were plotted (curve 1). The influence of calcium ions on the liquid phase pH is visible at low $\text{NH}_{3(g)}$ concentrations. This influence is the greater the higher Ca(II) ion concentrations are and the lower $\text{NH}_{3(g)}$ concentrations are. At $\text{NH}_{3(g)}$ concentrations higher than $4 \cdot 10^{-3}$ ppm, the presence of calcium ions of concentrations up to $1 \cdot 10^{-2}$ mol/kg do not influence liquid phase pH. Cations of other alkali metals have a similar effect.

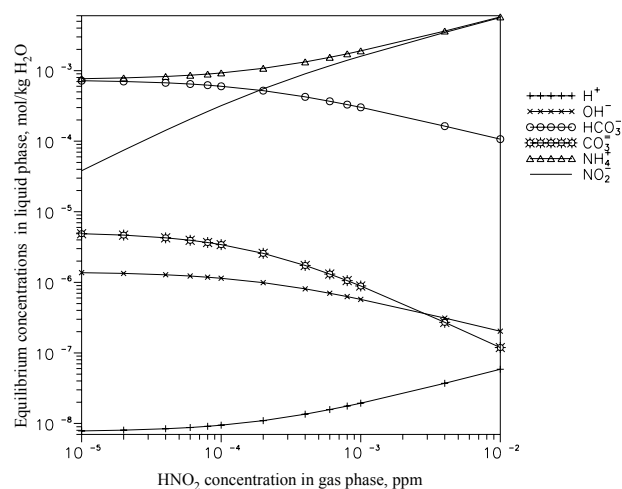


Fig. 3. Effect of HNO_2 concentration in the gas phase on the equilibrium composition of the liquid phase at other gaseous species concentrations: $\text{NH}_3 - 1$ ppm, $\text{CO}_2 - 350$ ppm.

Generalization

Based on the equations which constitute the thermodynamic model of a multicomponent gas-liquid system and assuming that strong and nonvolatile bases present in the system are practically totally dissociated, the general equation for hydrogen ion concentration as a function of partial pressures of gaseous components in the open atmospheric systems of type $\text{NH}_3 - \text{strong acids} - \text{strong bases} - \text{weak acids} - \text{CO}_2 - \text{H}_2\text{O}$ was derived:

$$m_H^3 - \frac{K_w \sum_i (zm_B)_i}{K_w + K_{N(-III)} K_{NH_3}^H p_{NH_3}} m_H^2 - \frac{K_w \left(\sum_i K_{H_i} K_i^H p_i + K_w \right)}{K_w + K_{N(-III)} K_{NH_3}^H p_{NH_3}} m_H - \frac{2K_w \sum_i K_{H_i} K_{H_i} K_i^H p_i}{K_w + K_{N(-III)} K_{NH_3}^H p_{NH_3}} = 0 \quad (6)$$

where m_B denotes molal concentration of cations coming from strong bases (e.g. Ca^{2+} , Mg^{2+} , Na^+ , K^+).

The equilibrium constants K in the above equation are expressed in terms of concentrations. The constants K are related to thermodynamic equilibrium constants K_a (expressed in terms of activities) by the equation:

$$K = \frac{K_a}{\prod \gamma_{m_i}^{\nu_i}} \quad (7)$$

For diluted solutions $K \approx K_a$.

The equation (6) is a cubic one in m_H , independently of the number of gaseous components. It is valid for not strongly alkaline solutions ($\text{pH} < 9.4$), when it may be

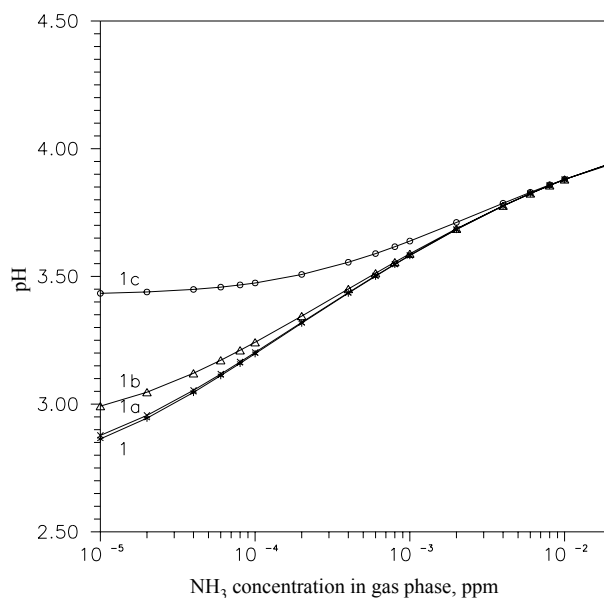


Fig. 4. The liquid phase pH as a function of NH_3 gas-phase concentration for the Ca(II) - H_2SO_4 - HNO_3 - CO_2 - H_2O system. Concentrations of gaseous components: $\text{H}_2\text{SO}_4 - 1 \cdot 10^{-18}$ ppm, $\text{HNO}_3 - 1 \cdot 10^{-6}$ ppm, $\text{CO}_2 - 350$ ppm. Concentrations of Ca(II) in the liquid phase: 1 - $m_{\text{Ca(II)}} = 0$ mol/kg, 1a - $m_{\text{Ca(II)}} = 1 \cdot 10^{-4}$ mol/kg, 1b - $m_{\text{Ca(II)}} = 1 \cdot 10^{-3}$ mol/kg, 1c - $m_{\text{Ca(II)}} = 1 \cdot 10^{-2}$ mol/kg.

assumed that strong bases present in the aqueous phase presented by general formula $B(OH)_z$ (where $z=1$ or 2) are totally dissociated.

Having the equilibrium concentration of hydrogen ions in the liquid phase, we can easily calculate equilibrium concentrations of the other liquid phase species using the expressions for appropriate equilibrium constants.

The equation (6) made it possible to analyze the effect of acidic gases on the hydrogen ion concentration and thus on the equilibrium composition of the solution. Species j can be neglected in the sum $\sum K_{1i} K_i^H p_i$ when at least for one of the other species, e.g. for k , the condition

$$K_{1j} K_j^H p_j < 0.01 \delta K_{1k} K_k^H p_k \quad (8)$$

is satisfied, and in the sum $\sum K_{1i} K_{2i} K_i^H p_i$ when

$$K_{1j} K_{2j} K_j^H p_j < 0.01 \delta K_{1k} K_{2k} K_k^H p_k \quad (9)$$

where δ denotes change in the sum value (in percentage) due to neglect of the species j .

The analysis of errors due to changes in the values of $\sum K_{1i} K_i^H p_i$ and $\sum K_{1i} K_{2i} K_i^H p_i$ showed that assumption of $\delta < 1.8\%$ do not cause an error in calculations of hydrogen ion concentration greater than 1%. If we make do with the error in calculations of hydrogen ion concentration up to 3%, we can assume greater values of δ , even up to 5%.

If the species j is a monoprotic acid it has no effect on hydrogen ion concentration when condition (8) is satisfied. If species j is a diprotic acid it has no effect on hydrogen ion concentration when both conditions (8) and (9) are satisfied.

Assuming approximately that activity coefficients of ions of the same valence are equal and that activity coefficients of neutral molecules are also equal the equilibrium constants K expressed in terms of concentrations can be replaced by the thermodynamic equilibrium constants K_a . By such proceeding the criteria of neglecting the effect of a given gas on the liquid phase hydrogen ion concentration were determined. These criteria are listed in Table 2. A given gas can be neglected with an error smaller than 1%, when at least one of the criteria (for this gas) listed in Table 2 is satisfied (in the case of diprotic acids at least one of the criteria in each column must be satisfied).

Using criteria from Table 2 the analysis was made in order to determine conditions under which individual gaseous pollutants have an effect on the equilibrium composition of the atmospheric water. The analysis was performed for concentrations of weak acid gases from upper limits of their ambient concentrations, i.e. $SO_2 - 1$ ppm, $CO_2 - 350$ ppm, HNO_2 and $HCOOH$ as well as $CH_3COOH - 0.02$ ppm.

It was found that the SO_2 and $HCOOH$ effect can exhibit only when strong acid gas concentrations satisfy the following conditions: $p_{H_2SO_4} < 5.4 \cdot 10^{-17}$ ppm, $p_{HNO_3} < 4.4 \cdot 10^{-7}$ ppm, $p_{HCl} < 7.1 \cdot 10^{-7}$ ppm. Gaseous HNO_2 and

CH_3COOH can have an effect on the liquid phase equilibrium composition if $p_{H_2SO_4} < 2.0 \cdot 10^{-18}$ ppm, $p_{HNO_3} < 4.4 \cdot 10^{-8}$ ppm, $p_{HCl} < 7.1 \cdot 10^{-8}$ ppm, and additionally for HNO_2 : $p_{SO_2} < 3.3 \cdot 10^{-2}$ ppm. Gaseous CO_2 will have an effect if $p_{H_2SO_4} < 2.2 \cdot 10^{-20}$ ppm, $p_{HNO_3} < 1.7 \cdot 10^{-10}$ ppm, $p_{HCl} < 2.9 \cdot 10^{-10}$ ppm, $p_{SO_2} < 3.5 \cdot 10^{-2}$ ppm, $p_{HNO_2} < 2.1 \cdot 10^{-2}$ ppm, $p_{HCOOH} < 8.0 \cdot 10^{-4}$ ppm, $p_{CH_3COOH} < 6.0 \cdot 10^{-13}$ ppm.

For each gas all the conditions must be fulfilled. Even if only one of the conditions for a given gas is not satisfied, the effect of this gas on the liquid phase equilibrium composition can be neglected.

Equation (6) as well as that derived from it criteria (8) and (9) make it possible to obtain, with very small expenditure of work and time, exact and detailed information on the effect of acid gas pollutants on liquid phase pH and equilibrium composition in the open atmospheric gas-liquid systems.

Equation (6), in spite of being cubic, is very useful. This equation makes the analysis of chemical equilibria in complex atmospheric gas-liquid systems considerably easier. This equation permits us to estimate which acid gases have no effect on hydrogen ion concentration under examined conditions. Owing to this fact, the analysis of a complex system can be reduced to the analysis of a simpler one. Even if it is necessary to solve numerically a system of equations composing the complete thermodynamic model, equation (6) can be of great service because it makes it possible to eliminate the species that do not affect the hydrogen ion concentration which leads to a reduction in the number of equations to solve and consequently to a reduction both in difficulty and time of calculations. Therefore, this equation can also be convenient to apply in mathematical models of dynamic processes occurring in the polluted atmosphere. The necessary element in these models is calculation of equilibrium concentrations of individual species in each time step, because this is what determines the driving forces, and so the rates of the processes.

Conclusions

The results of the performed thermodynamic analysis of open multicomponent gas-liquid atmospheric systems permit us to formulate the following conclusions:

1. The derived general equation (6) together with the criteria (8) and (9) of neglecting the effect of acid gas pollutants on the liquid phase equilibrium composition constitute an effective and easy-to-use tool for examination and interpretation of equilibria in complex open gas-liquid atmospheric systems of the type NH_3 -strong bases-strong acids-weak acids- CO_2 - H_2O . These equations can also be useful for mathematical modelling of dynamic processes taking place in the polluted atmosphere because they simplify calculations of driving forces of these processes.
2. The effect of acid gas j on the pH and equilibrium composition of the liquid phase in open atmospheric

Table 2. Criteria of neglecting the effect of major acid gas pollutants on liquid phase composition and pH.

Gas	Criteria from Eq. (8)	Criteria from Eq. (9)
CO ₂	$p_{H_2SO_4} > 6.16 \cdot 10^{-23} p_{CO_2}$ $p_{HNO_3} > 5.01 \cdot 10^{-13} p_{CO_2}$ $p_{SO_2} > 1.01 \cdot 10^{-4} p_{CO_2}$ $p_{HNO_2} > 6.12 \cdot 10^{-5} p_{CO_2}$ $p_{HCl} > 8.18 \cdot 10^{-13} p_{CO_2}$ $p_{HCOOH} > 2.30 \cdot 10^{-6} p_{CO_2}$ $p_{CH_3COOH} > 1.7 \cdot 10^{-5} p_{CO_2}$	$p_{H_2SO_4} > 2.81 \cdot 10^{-31} p_{CO_2}$ $p_{SO_2} > 7.20 \cdot 10^{-8} p_{CO_2}$
SO ₂	$p_{CO_2} > 9.89 \cdot 10^7 p_{SO_2}$ $p_{H_2SO_4} > 6.09 \cdot 10^{17} p_{SO_2}$ $p_{HNO_3} > 4.95 \cdot 10^7 p_{SO_2}$ $p_{HNO_2} > 6.05 \cdot 10^1 p_{SO_2}$ $p_{HCl} > 8.09 \cdot 10^{-7} p_{SO_2}$ $p_{HCOOH} > 2.27 p_{SO_2}$ $p_{CH_3COOH} > 1.68 \cdot 10^1 p_{SO_2}$	$p_{CO_2} > 1.39 \cdot 10^{11} p_{SO_2}$ $p_{H_2SO_4} > 3.90 \cdot 10^{22} p_{SO_2}$
H ₂ SO ₄	$p_{CO_2} > 1.62 \cdot 10^{26} p_{H_2SO_4}$ $p_{SO_2} > 1.64 \cdot 10^{20} p_{H_2SO_4}$ $p_{HNO_3} > 8.13 \cdot 10^{11} p_{H_2SO_4}$ $p_{HNO_2} > 9.94 \cdot 10^{19} p_{H_2SO_4}$ $p_{HCl} > 1.33 \cdot 10^{12} p_{H_2SO_4}$ $p_{HCOOH} > 3.73 \cdot 10^{18} p_{H_2SO_4}$ $p_{CH_3COOH} > 2.76 \cdot 10^{19} p_{H_2SO_4}$	$p_{CO_2} > 3.56 \cdot 10^{34} p_{H_2SO_4}$ $p_{SO_2} > 2.56 \cdot 10^{25} p_{H_2SO_4}$
HNO ₃	$p_{CO_2} > 2.00 \cdot 10^{16} p_{HNO_3}$ $p_{SO_2} > 2.02 \cdot 10^{10} p_{HNO_3}$ $p_{H_2SO_4} > 1.23 \cdot 10^{-8} p_{HNO_3}$ $p_{HNO_2} > 1.22 \cdot 10^{10} p_{HNO_3}$ $p_{HCl} > 1.63 \cdot 10^2 p_{HNO_3}$ $p_{HCOOH} > 4.59 \cdot 10^8 p_{HNO_3}$ $p_{CH_3COOH} > 3.39 \cdot 10^9 p_{HNO_3}$	-
HNO ₂	$p_{CO_2} > 1.63 \cdot 10^8 p_{HNO_2}$ $p_{SO_2} > 1.65 \cdot 10^2 p_{HNO_2}$ $p_{H_2SO_4} > 1.01 \cdot 10^{-16} p_{HNO_2}$ $p_{HNO_3} > 8.18 \cdot 10^{-7} p_{HNO_2}$ $p_{HCl} > 1.34 \cdot 10^{-6} p_{HNO_2}$ $p_{HCOOH} > 3.75 p_{HNO_2}$ $p_{CH_3COOH} > 2.78 \cdot 10^1 p_{HNO_2}$	-
HCl	$p_{CO_2} > 1.22 \cdot 10^{16} p_{HCl}$ $p_{SO_2} > 1.24 \cdot 10^{10} p_{HCl}$ $p_{H_2SO_4} > 7.53 \cdot 10^{-9} p_{HCl}$ $p_{HNO_3} > 6.12 \cdot 10^1 p_{HCl}$ $p_{HNO_2} > 7.48 \cdot 10^9 p_{HCl}$ $p_{HCOOH} > 2.81 \cdot 10^8 p_{HCl}$ $p_{CH_3COOH} > 2.08 \cdot 10^9 p_{HCl}$	-
HCOOH	$p_{CO_2} > 4.35 \cdot 10^9 p_{HCOOH}$ $p_{SO_2} > 4.40 \cdot 10^3 p_{HCOOH}$ $p_{H_2SO_4} > 2.68 \cdot 10^{15} p_{HCOOH}$ $p_{HNO_3} > 2.18 \cdot 10^{-5} p_{HCOOH}$ $p_{HNO_2} > 2.67 \cdot 10^3 p_{HCOOH}$ $p_{HCl} > 3.65 \cdot 10^{-5} p_{HCOOH}$ $p_{CH_3COOH} > 7.40 \cdot 10^2 p_{HCOOH}$	-
CH ₃ COOH	$p_{CO_2} > 5.88 \cdot 10^8 p_{CH_3COOH}$ $p_{SO_2} > 5.95 \cdot 10^2 p_{CH_3COOH}$ $p_{H_2SO_4} > 3.62 \cdot 10^{-16} p_{CH_3COOH}$ $p_{HNO_3} > 2.95 \cdot 10^{-6} p_{CH_3COOH}$ $p_{HNO_2} > 3.60 \cdot 10^2 p_{CH_3COOH}$ $p_{HCl} > 4.81 \cdot 10^{-6} p_{CH_3COOH}$ $p_{HCOOH} > 1.35 \cdot 10^1 p_{CH_3COOH}$	-

systems can be neglected with error smaller than δ if at least in respect of one of the other acid gases (i.e. k) the following criteria are satisfied:

$$K_j K_j^H p_j < 0.01 \delta K_{1k} K_k^H p_k$$

$$K_j K_{2j} K_j^H p_j < 0.01 \delta K_{1k} K_{2k} K_k^H p_k$$

If j is a monoprotic acid the first criterion must be satisfied, and if j is a diprotic acid both conditions must be satisfied.

- The greatest effect on the liquid phase equilibrium composition in open atmospheric systems have $\text{NH}_{3(g)}$, $\text{H}_2\text{SO}_{4(g)}$, $\text{HNO}_{3(g)}$ and $\text{HCl}_{(g)}$, from which the decisive effect have $\text{NH}_{3(g)}$ and $\text{H}_2\text{SO}_{4(g)}$. The effect of $\text{HNO}_{3(g)}$ and $\text{HCl}_{(g)}$ becomes comparable with that of $\text{NH}_{3(g)}$ and $\text{H}_2\text{SO}_{4(g)}$ only at low enough concentrations of $\text{NH}_{3(g)}$ and/or $\text{H}_2\text{SO}_{4(g)}$.
- The effect of $\text{SO}_{2(g)}$ (at concentration < 1 ppm) and $\text{HCOOH}_{(g)}$ (at concentration < 0.02 ppm) on the pH and equilibrium composition of the liquid phase in open atmospheric systems can be visible only when concentrations of strong acids in the gas phase satisfy the conditions: $p_{\text{H}_2\text{SO}_4} < 5.4 \cdot 10^{-17}$ ppm, $p_{\text{HNO}_3} < 4.4 \cdot 10^{-7}$ ppm, $p_{\text{HCl}} < 7.1 \cdot 10^{-7}$ ppm.
- $\text{HNO}_{2(g)}$ and $\text{CH}_3\text{COOH}_{(g)}$ (at concentrations < 0.02 ppm) can affect the pH and equilibrium composition of the liquid phase only when $p_{\text{H}_2\text{SO}_4} < 2.0 \cdot 10^{-18}$ ppm, $p_{\text{HNO}_3} < 1.6 \cdot 10^{-8}$ ppm, $p_{\text{HCl}} < 2.7 \cdot 10^{-8}$ ppm, and for $\text{HNO}_{2(g)}$ one more condition must be satisfied: $p_{\text{SO}_2} < 3.3 \cdot 10^{-2}$ ppm.
- The effect of $\text{CO}_{2(g)}$ on the pH and equilibrium composition of the liquid phase in open atmospheric systems can be visible only when $p_{\text{H}_2\text{SO}_4} < 2.2 \cdot 10^{-20}$ ppm, $p_{\text{HNO}_3} < 1.7 \cdot 10^{-10}$ ppm, $p_{\text{HCl}} < 2.9 \cdot 10^{-10}$ ppm, $p_{\text{SO}_2} < 3.5 \cdot 10^{-2}$ ppm, $p_{\text{HNO}_2} < 2.1 \cdot 10^{-2}$ ppm, $p_{\text{HCOOH}} < 8.0 \cdot 10^{-4}$ ppm, $p_{\text{CH}_3\text{COOH}} < 6.0 \cdot 10^{-3}$ ppm.
- Cations of alkali metals have influence on the pH and equilibrium composition of the liquid phase only at low NH_3 concentrations in the gas phase. At $\text{NH}_{3(g)}$ concentrations higher than $4 \cdot 10^{-3}$ ppm the presence of alkali metal cations at concentrations up to $1 \cdot 10^{-2}$ mol/kg does not affect the liquid phase pH and equilibrium composition.

It should be noted that the above conclusions are justified for the open systems (of approximately constant partial pressures of gaseous pollutants), in which depletion of a component in the gas phase due to its absorption in atmospheric water droplets is slight. Such systems may occur under the conditions of the stationary state between emissions and/or production of gaseous pollutants in the atmosphere and their removal from the gas phase or at very low the liquid water content, typical of aerosols. Under different conditions atmospheric gas-liquid systems should be approximated by a closed system or an intermediate system between an open and a closed one, i.e. a system which is open with respect to some components

and closed with respect to others. The analysis of acid-base equilibria in such systems will be the subject of a separate article.

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