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 NH₃ – strong bases – strong acids – weak acids – CO₂ – H₂O. 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 NH₃ – strong bases – strong acids – weak acids – CO₂ – H₂O.

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 SO₂ and NOₓ 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-
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 NH₃ – strong bases – strong acids – weak acids – CO₂ – H₂O.

### 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:

\[
K_{iA}(T, \rho) = \frac{a_i}{a_j^*} = \frac{m_{iA}}{m_{jA}} \quad (i = 1, ..., 9) \quad (1)
\]

\[
K_{iA}(T, \rho) = \left( \frac{m_i^*}{m_j^*} \right)^{\gamma_{mi}} = \left( \frac{m_i^*}{m_j^*} \right)^{\gamma_{mi}} \quad (2)
\]

\[
m_{iA} = \sum_{m=i} m_{m} + \sum_{i} m_{iA} \quad (3)
\]

\[
\sum_{i} n_i = 0 \quad (4)
\]

where: \( K_{iA}(T, \rho) \) - thermodynamic equilibrium constant for \( l_i \leftrightarrow l_j \), \( K_{iA}(T, \rho) \) - thermodynamic equilibrium constant for \( f_i \leftrightarrow f_j \) 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, \( a_{ij} \) - pressure activity of species \( j \) in the gas phase, \( a_{ik} \) - molar activity of species \( i \) in the liquid phase, \( p_i \) - partial pressure of species \( i \), \( m_i \) - molal concentration of species \( i \), mol/kg H₂O, \( \gamma_{mi} \) - molar activity coefficient of species \( i \) in the liquid phase, \( p_i^* \), \( m_i^* \) - pressure and concentration in standard state, respectively (\( p_i^* = 1 \) bar, \( m_i^* = 1 \) mol/kg H₂O), \( \nu_j \) - stoichiometric coefficient of species \( i \) in reaction \( j \), \( m_{iA} \) - total concentration of species \( A \) (sum of the concentrations of ionic and molecular forms) in the solution, mol/kg H₂O, \( \sum_{m=i} m_{m} \) - concentration of molecular species \( A \) in the solution, mol/kg H₂O, \( \sum_{i} m_{iA} \) - concentration of ionic species \( A \) in the solution, mol/kg H₂O, \( \gamma_i \) - charge of ion \( i \).
Under atmospheric conditions the gas may be assumed ideal and then it may be assumed that \( \gamma_i = p_i \). Molal activity coefficients \( \gamma_i \) were calculated by an equation derived from Pitzer’s theory [14 – 16]:

\[
\ln \gamma_i = -A_i \sum_{j=1}^{N} \frac{z_j^2}{z_i^2} \left(1 - \frac{z_j}{z_i} \right) + \frac{z_i}{z_j} \sum_{j=1}^{N} \frac{z_j}{z_i} \ln \frac{z_i}{z_j} \left(1 - \frac{z_j}{z_i} \right) + \frac{z_i}{z_j} \sum_{j=1}^{N} \frac{z_j}{z_i} \ln \frac{z_j}{z_i} \left(1 - \frac{z_j}{z_i} \right)
\]

where \( A_i \) is the Debye–Hückel constant, \( I \) is the ionic strength of the solution, \( \alpha_i \) has the value 2.0 for 1-1 and 2-1 electrolytes (terms with \( \alpha_i \) are omitted), for 2-2 electrolytes \( \alpha_i = 1.4 \) and \( \alpha_i = 12.0 \), \( b = 1.2 \) for all electrolytes, \( \beta^{\alpha i}, \beta^{\beta i}, \beta^{\gamma i} \) - 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]. Equilibrium 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: \( \text{NH}_3, \text{H}_2\text{SO}_4, \text{HNO}_3, \text{HCl}, \text{HNO}_2, \text{SO}_3 \), and \( \text{CO}_2 \). In order to determine their effect on composition and \( \text{pH} \) 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 \( \text{NH}_3 \) gas-phase concentration have a considerable effect on the ionic composition and \( \text{pH} \) of atmospheric water.

<p>| Table 1. Thermodynamic equilibrium constants at 298.15 K. |</p>
<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>( K_{\alpha} ) or ( K' )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3\text{H}_2\text{O} \leftrightarrow \text{NH}_4\cdot\text{H}_2\text{O} )</td>
<td>55.74</td>
<td>[19]</td>
</tr>
<tr>
<td>( \text{NH}_3\text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- )</td>
<td>1.774 \cdot 10^{-5}</td>
<td>[20]</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4(w) \leftrightarrow \text{H}_2\text{SO}_4(aq) )</td>
<td>2.484 \cdot 10^{-1}</td>
<td>*</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4(aq) \leftrightarrow \text{H}^+ + \text{HSO}_4^- )</td>
<td>1000.0</td>
<td>[21]</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4(aq) \leftrightarrow \text{H}^+ + \text{SO}_4^{2-} )</td>
<td>1.03 \cdot 10^{-2}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{HNO}_3(aq) \leftrightarrow \text{H}^+ + \text{NO}_3^- )</td>
<td>1.983 \cdot 10^{1}</td>
<td>[13]</td>
</tr>
<tr>
<td>( \text{HNO}_3(aq) \leftrightarrow \text{H}^+ + \text{NO}_3^- )</td>
<td>15.4</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{HNO}_3(aq) \leftrightarrow \text{H}^+ + \text{NO}_3^- )</td>
<td>49</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{HNO}_3(aq) \leftrightarrow \text{H}^+ + \text{NO}_3^- )</td>
<td>5.1 \cdot 10^{4}</td>
<td>[23]</td>
</tr>
<tr>
<td>( \text{HCl}(g) \leftrightarrow \text{HCl}(aq) )</td>
<td>1.1</td>
<td>[24]</td>
</tr>
<tr>
<td>( \text{HCl}(aq) \leftrightarrow \text{H}^+ + \text{Cl}^- )</td>
<td>1.7 \cdot 10^{4}</td>
<td>[24]</td>
</tr>
<tr>
<td>( \text{SO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O} )</td>
<td>1.23</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{SO}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4(aq) + \text{H}^+ )</td>
<td>1.23 \cdot 10^{-2}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{HSO}_4^- \leftrightarrow \text{SO}_4^{2-} + \text{H}^+ )</td>
<td>6.6 \cdot 10^{-4}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 \cdot \text{H}_2\text{O} )</td>
<td>3.4 \cdot 10^{-2}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 )</td>
<td>4.5 \cdot 10^{-5}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ )</td>
<td>4.7 \cdot 10^{-11}</td>
<td>[22]</td>
</tr>
<tr>
<td>( \text{HCOOH}(aq) \leftrightarrow \text{HCOOH}(aq) )</td>
<td>3.7 \cdot 10^{4}</td>
<td>[25]</td>
</tr>
<tr>
<td>( \text{CH}_2\text{COOH}(aq) \leftrightarrow \text{H}^+ + \text{H}_2\text{COO}^- )</td>
<td>1.8 \cdot 10^{4}</td>
<td>[25]</td>
</tr>
<tr>
<td>( \text{CH}_2\text{COOH}(aq) \leftrightarrow \text{H}^+ + \text{CH}_2\text{COO}^- )</td>
<td>5.0 \cdot 10^{5}</td>
<td>[25]</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- )</td>
<td>1.008 \cdot 10^{-14}</td>
<td>[20]</td>
</tr>
</tbody>
</table>

*For \( K_{\alpha} \) for \( \text{H}_2\text{SO}_4 \) has been calculated on the basis of the equilibrium constants for \( \text{H}_2\text{SO}_4(aq) \leftrightarrow \text{H}^+ + \text{HSO}_4^- \) [26] and \( \text{H}_2\text{SO}_4(aq) \leftrightarrow \text{H}^+ + \text{H}_2\text{O} \) [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 NH₃ gas-phase concentration for the following concentrations of other gaseous constituents: SO₂ - 1 ppm, H₂SO₄ - 2.5·10⁻¹⁸ ppm, HNO₂ - 10⁻⁶ ppm, HNO₃ - 10⁻⁵ ppm, CO₂ - 350 ppm. The NH₃ gas-phase concentration was changed over a wide (from the atmospheric point of view) range from 1·10⁻⁴ ppm up to 0.1 ppm. At very low NH₃ gas-phase concentration (≤ 10⁻⁴ ppm) the predominant species in the aqueous phase are NH₄⁺, H⁺, NO₃⁻ and SO₄²⁻ ions. As gaseous NH₃ concentration increases, hydrogen ion concentration decreases, whereas NH₄⁺, SO₄²⁻ and NO₃⁻ concentrations increase. SO₄²⁻ concentration increases more strongly than NO₃⁻ concentration. Thus, at higher gaseous NH₃ concentrations (above 10⁻⁵ ppm), predominant species in the solution are NH₄⁺, H⁺, NO₃⁻ and SO₄²⁻ ions. As gaseous NH₃ concentration increases, hydrogen ion concentration decreases, whereas NH₄⁺, SO₄²⁻ and NO₃⁻ concentrations increase. SO₄²⁻ concentration increases more strongly than NO₃⁻ concentration. Thus, at higher gaseous NH₃ concentrations (above 10⁻⁵ ppm), predominant species in the solution are NH₄⁺, H⁺, NO₃⁻ and SO₄²⁻ ions. Despite increasing NH₃(g) 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 SO₂ 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 SO₂ gas-phase concentration was being changed from 10⁻⁶ ppm to 1 ppm with the following assumed concentrations of the other gas phase components: NH₃ - 1 ppm, CO₂ - 350 ppm, HNO₂ - 10⁻⁶ ppm.

If SO₂ concentration is lower than 10⁻⁵ ppm, NH₄⁺ and HCO₃⁻ ions are major species in the solution and their concentrations are practically the same. Within this range, HSO₄⁻ and SO₄²⁻ concentrations are much lower than those of NH₄⁺ and HCO₃⁻. However, as gaseous SO₂ concentration increases, HSO₄⁻ and SO₄²⁻ concentrations also increase while HCO₃⁻ concentration falls. As a result, HCO₃⁻, HSO₄⁻ and SO₄²⁻ concentrations are approximately of the same order within the range of SO₂ concentrations of 10⁻³ - 10⁻² ppm. At still higher SO₂ concentrations (above 10⁰ ppm) the major species in the aqueous phase besides NH₄⁺ are HSO₄⁻ and SO₄²⁻ ions, and HCO₃⁻ ion concentration is not of great importance. SO₄²⁻ ion concentration is higher than HSO₄⁻ concentration up to the gas phase SO₂ concentration of about 10⁻³ ppm. At higher SO₂ concentrations HSO₄⁻ ions predominate over SO₄²⁻ ions. With SO₂ concentrations ranging from 10⁶ to 1 ppm, the liquid phase pH changes from 8.13 to 6.30.

NO₂⁻ ion concentration is very low within the whole range of SO₂(g) concentrations. It follows that gaseous HNO₂ practically has no effect on the aqueous phase equilibrium if its concentration is lower than about 10⁶ ppm. However, the effect of HNO₂ on H⁺ ion concentration in the presence of SO₂ cannot finally be excluded at higher HNO₂ concentration. Due to the low pH range, HCO₃⁻ concentrations because dissociation constants for HNO₂ and SO₂ differ only about 24 times.

Fig. 3 presents the results of calculations performed with an assumption that in the gas phase are present only NH₃ at concentration of 1 ppm, CO₂ at 350 ppm and HNO₂ at varied concentrations of 1·10⁻⁴ - 1·10⁻² ppm. At gaseous HNO₂ concentration below 10⁻³ ppm the dominant species in the liquid phase are NH₄⁺ and HCO₃⁻ ions and their concentrations are practically equal. In this range HNO₂ does not affect the liquid phase equilibrium composition, in spite of high NH₃(g) concentration.
Acid-Base Equilibria in Open Atmospheric...

(1 ppm) – alkaline component, which increases HNO₂ solubility in the solution.

With the increase in HNO₂ concentration above 10⁻⁵ ppm, HCO₃⁻ concentration drops and NH₄⁺ concentration rises. NO₂⁻ ion concentration also rises and at HNO₂ concentration equal to or higher than 10⁻³ ppm NO₂⁻ concentration is practically the same as NH₄⁺ concentration. HCO₃⁻ ion is not the main species any longer. It is replaced by NO₂⁻ ion.

Gaseous HNO₂ 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 NH₃ on the equilibrium composition and pH of the aqueous phase, calculations were made for the system where Ca²⁺ 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: 1·10⁻⁴, 1·10⁻³ and 1·10⁻² mol/kg and for the following gas phase composition: H₂SO₄ - 1·10⁻¹⁸ ppm, HNO₃ - 1·10⁻⁶ ppm, CO₂ – 350 ppm. NH₃ concentration in the gas phase was being changed from 1·10⁻⁵ ppm to 2·10⁻² 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 NH₃(g) concentrations. This influence is the greater the higher Ca(II) ion concentrations are and the lower NH₃(g) concentrations are. At NH₃(g) concentrations higher than 4·10⁻³ ppm, the presence of calcium ions of concentrations up to 1·10⁻² mol/kg do not influence liquid phase pH. Cations of other alkali metals have a similar effect.

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 NH₃ – strong acids – strong bases – weak acids – CO₂ – H₂O was derived:

\[
\begin{align*}
\frac{m_H^+}{m_{H^+}} & = K_p \left( \frac{m_{NH_3} \cdot \sum m_{Acid} \cdot m_{Base}^{k_{Acid}}} {m_{NH_3} + \sum m_{Acid} \cdot m_{Base}^{k_{Acid}}} \right)
\end{align*}
\]

where \(m_j\) denotes molal concentration of cations coming from strong bases (e.g. Ca²⁺, Mg²⁺, 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:

\[
K = \frac{K_a}{[H^+]_{ref}}
\]

For diluted solutions \(K = K_a\).

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 (\(pH < 9.4\)), when it may be

Fig. 3. Effect of HNO₂ concentration in the gas phase on the equilibrium composition of the liquid phase at other gaseous species concentrations: NH₃ - 1 ppm, CO₂ - 350 ppm.

Fig. 4. The liquid phase pH as a function of NH₃ gas-phase concentration for the Ca(II) - H₂SO₄ - HNO₃ - CO₂ - H₂O system. Concentrations of gaseous components: H₂SO₄ - 1·10⁻¹⁸ ppm, HNO₃ - 1·10⁻⁶ ppm, CO₂ - 350 ppm. Concentrations of Ca(II) in the liquid phase: 1 - \(m_{calc} = 0\) mol/kg, 1a - \(m_{calc} = 1\) mol/kg, 1b - \(m_{calc} = 1\) mol/kg, 1c - \(m_{calc} = 1\) 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 concentration equilibrium 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 \(\sum K_i K_i^j p_j\) when at least for one of the other species, e.g. for \(k\), the condition

\[ K_i K_i^j p_j < 0.01 \delta K_i K_i^j p_k \]  

is satisfied, and in the sum \(\sum K_i K_i^j p_j\) when

\[ K_i K_i^j p_j < 0.01 \delta K_i K_i^j p_k \]  

where \(\delta\) 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 \(\sum K_i K_i^j p_j\) and \(\sum K_i K_i^j p_k\) 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 \(\delta\), 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 \(K_i\). 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\(_3\)COOH – 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: \(P_{\text{HgSO}_2} < 5.4 \times 10^{-7}\) ppm, \(P_{\text{HNO}_2} < 4.4 \times 10^{-7}\) ppm, \(P_{\text{HCOOH}} < 7.1 \times 10^{-9}\) ppm. Gaseous HNO\(_2\) and CH\(_3\)COOH can have an effect on the liquid phase equilibrium composition if \(P_{\text{HgSO}_2} < 2.0 \times 10^{-18}\) ppm, \(P_{\text{HgNO}_2} < 4.4 \times 10^{-10}\) ppm, \(P_{\text{HNO}_2} < 4.4 \times 10^{-8}\) ppm, \(P_{\text{HCOOH}} < 3.3 \times 10^{-2}\) ppm. Gaseous HNO\(_2\) will have an effect if \(P_{\text{HgSO}_2} < 2.2 \times 10^{-20}\) ppm, \(P_{\text{HgNO}_2} < 1.7 \times 10^{-16}\) ppm, \(P_{\text{HNO}_2} < 2.9 \times 10^{-10}\) ppm, \(P_{\text{HCOOH}} < 3.5 \times 10^{-10}\) ppm, \(P_{\text{HCOOH}} < 2.1 \times 10^{-2}\) ppm, \(P_{\text{HCOOH}} < 8.0 \times 10^{-4}\) ppm, \(P_{\text{CH}_3\text{COOH}} < 6.0 \times 10^{-10}\) 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\(_2\)O. 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.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Criteria from Eq. (8)</th>
<th>Criteria from Eq. (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>( p_{\text{H}<em>2\text{SO}<em>3} &gt; 6.16 \cdot 10^{-2} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{HNO}<em>3} &gt; 5.01 \cdot 10^{-2} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{SO}<em>2} &gt; 1.01 \cdot 10^{-4} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{H}<em>2\text{SO}<em>3} &gt; 6.12 \cdot 10^{-4} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{HCl}} &gt; 8.18 \cdot 10^{-15} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{HCOOH}} &gt; 2.30 \cdot 10^{-9} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{CH}<em>3\text{COOH}} &gt; 1.7 \cdot 10^{4} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{H}<em>2\text{SO}<em>3} &gt; 2.81 \cdot 10^{-31} \ p</em>{\text{CO}<em>2} ) ( p</em>{\text{HCl}} &gt; 7.20 \cdot 10^{-8} \ p</em>{\text{CO}_2} )</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>( p_{\text{CO}<em>2} &gt; 9.89 \cdot 10^{-9} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{H}<em>2\text{SO}<em>3} &gt; 6.09 \cdot 10^{-11} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{HNO}<em>3} &gt; 4.95 \cdot 10^{-11} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{H}<em>2\text{SO}<em>3} &gt; 6.05 \cdot 10^{-11} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{HCl}} &gt; 8.09 \cdot 10^{-11} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{HCOOH}} &gt; 2.27 \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{CH}<em>3\text{COOH}} &gt; 1.68 \cdot 10^{-4} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{CO}<em>2} &gt; 1.39 \cdot 10^{-14} \ p</em>{\text{SO}<em>2} ) ( p</em>{\text{H}_2\text{SO}<em>3} &gt; 3.90 \cdot 10^{-22} \ p</em>{\text{SO}_2} )</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td></td>
<td>( p_{\text{CO}<em>2} &gt; 3.56 \cdot 10^{-4} \ p</em>{\text{H}_2\text{SO}<em>4} ) ( p</em>{\text{SO}<em>2} &gt; 2.56 \cdot 10^{-22} \ p</em>{\text{H}_2\text{SO}_4} )</td>
</tr>
<tr>
<td>HNO₃</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>HNO₂</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>HCOOH</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CH₃COOH</td>
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</tbody>
</table>
systems can be neglected with error smaller than $\delta$ if at least in respect of one of the other acid gases (i.e. $k$) the following criteria are satisfied:

$$K_{1j}^ {-1} p_{j} < 0.01 \delta K_{1j}^ {-1} P_{h}$$

$$K_{2j}^ {-1} p_{j} < 0.01 \delta K_{2j}^ {-1} P_{h}$$

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

3. The greatest effect on the liquid phase equilibrium composition in open atmospheric systems have NH$_{4}$, H$_2$SO$_4$, HNO$_3$ and HCl from which the decisive effect have NH$_{4}$ and H$_2$SO$_4$. The effect of HNO$_3$ and HCl becomes comparable with that of NH$_{4}$ and H$_2$SO$_4$ only at low enough concentrations of NH$_{4}$ and/or H$_2$SO$_4$.

4. The effect of SO$_2(g)$ (at concentration < 1 ppm) and HCOOH$_{(aq)}$ (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: $p_{j}$ < 5.4·10$^{-17}$ ppm, $p_{j}$ < 4.4·10$^{-7}$ ppm, $p_{j}$ < 7.1·10$^{-11}$ ppm.

5. HNO$_3(g)$ and CH$_3$COOH$_{(aq)}$ (at concentrations < 0.02 ppm) can affect the pH and equilibrium composition of the liquid phase only when $p_{j}$ < 2.0·10$^{-18}$ ppm, $p_{j}$ < 1.6·10$^{-8}$ ppm, $p_{j}$ < 2.7·10$^{-8}$ ppm, and for HNO$_3(g)$ one more condition must be satisfied: $p_{j}$ < 3.3·10$^{-8}$ ppm.

6. The effect of CO$_2(g)$ on the pH and equilibrium composition of the liquid phase in open atmospheric systems can be visible only when $p_{j}$ < 2.2·10$^{-30}$ ppm, $p_{j}$ < 1.7·10$^{-10}$ ppm, $p_{j}$ < 2.9·10$^{-10}$ ppm, $p_{j}$ < 3.5·10$^{-2}$ ppm, $p_{j}$ < 2.1·10$^{-10}$ ppm, $p_{j}$ < 8.0·10$^{-10}$ ppm, $p_{j}$ < 6.0·10$^{-11}$ ppm.

7. Cations of alkali metals have influence on the pH and equilibrium composition of the liquid phase only at low NH$_4$ concentrations in the gas phase. At NH$_4$ concentrations higher than 4·10$^{-3}$ ppm the presence of alkali metal cations at concentrations up to 1·10$^{-2}$ 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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