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Removal of Gaseous Pollutants in Wet Atmosphere

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Abstract. Gaseous pollutants such as SO_2 and NO_x once emitted to the atmosphere is oxidized to sulphate and nitrate through gaseous and aqueous phase processes. The absorption and desorption of gaseous pollutants by water droplets is the beginning of the removal process of these gases. However, absorption and desorption involve a complex mechanism which incorporates dissolving and extraction of these species in and out of water droplets.

This paper will discuss the possible mechanism of absorption as an example of the behaviour of the atmospheric pollutants. Altough, Saudi Arabia has a dry atmosphere in general, the proposed phenomenon is an important one in the coastal cities specially in the summer.

Introduction

The removal of gaseous pollutants is the final step in a complex series of processes that involve many species in multi-phases. Atmospheric hydro-activities such as fog, rain and snow help in precipitating pollutant particles and absorbing gases. This process is called wet deposition. It plays an important role in removing gaseous pollutants from the atmosphere and forming the so called "acid deposition".

Fig. 1. shows possible different pathways for the disposition of atmospheric pollutants. These pathways are reversible and interchargable. A gaseous species could precipitate by the following steps.

1) Mix with water vapor or water droplets.
2) Attach to the water droplets.
3) React within the aqueous phase.
4) Deposit by gravity.

other processes such as condensation, coagulation and other physical and chemical processes may take place.

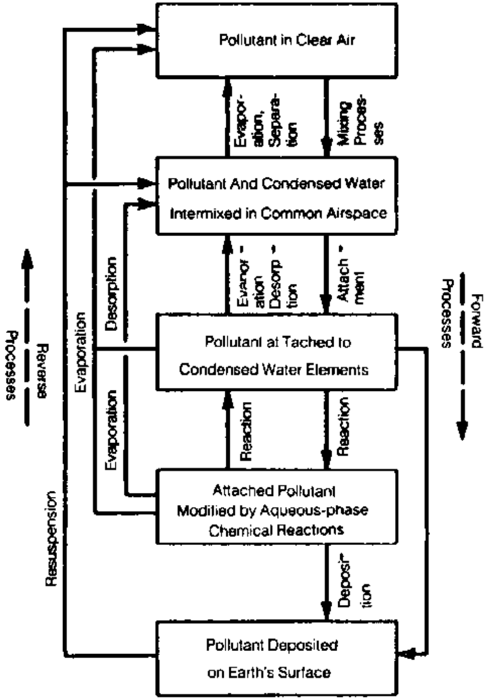


Fig. 1. Pathways for the disposition of atmospheric pollutants [5]

Through aqueous removal of SO_2 and NO_x, sulphuric and nitric acids, the two major contributors of acid rain, are formed. Their rates of formation and precipitation depend on the oxidation rates of SO_2 and NO_x in the atmosphere. Water content of the atmosphere, pH value, concentration of SO_2 and NO_x and presence of other species are examples of some important factors affecting the gaseous removal process. This paper gives a detailed discussion on the formation and deposition of SO_2 and NO_x wet processes.

Gas Phase Reactions

NO_x gases are emitted from combustion processes. Internal combustion engines are the major contributor of NO_x emissions. NO and NO_2 are the components of NO_x gases. Most of combustion-origin NO_x are NO. If small amounts of NO are present in the atmosphere, a series of complex photochemical reactions will be triggered. This will lead to the formation of various nitrogen containing species (*e.g.* NO_2, nitric acid, peroxy acetyl and nitrates) and production of ozone. Details of these gas phase reactions are found elsewhere [1].

In contrast to NO_x, SO_2 which is emitted mainly from petroleum refineries and electric power stations, undergoes little gas phase reaction. Photodissociation of SO_2 is not possible. Only light with a wavelength below 0.28 um (which does not penetrate into the troposphere) can photodissociate SO_2. Reactions of SO_2 with other gaseous species such as oxygen atoms and hydrocarbons are important. Only reactions with OH^- radicals may be significant with an average rate of 0.007 per hour in urban summer time [2].

Hydroxyl radicals may form in the atmosphere by the reaction of oxygen atoms with water vapor. Oxygen atoms are mainly formed by the photodissociation of ozone by ultraviolet radiation according to the following reactions:

$$O_3 \xrightarrow{h} O + O_2 \qquad (1)$$

$$O + H_2O \longrightarrow 2\,OH^- \qquad (2)$$

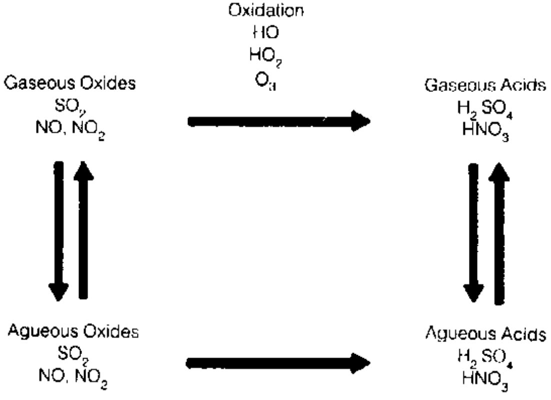


Fig. 2. Formation of sulfate and nitrate in the atmosphere.

As illustrated in Fig. 2, hydroxyl radicals help in converting SO_2 into sulphuric acid in a series of reactions which can be represented by the following:

$$SO_2 + OH + M \longrightarrow HOSO_2 + M \quad (3)$$

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3 \quad (4)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \quad (5)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad (6)$$

Atmospheric Water Content

The concentration of water vapor in the atmosphere is often given by relative humidity. At a certain ambient temperature, the relative humidity is defined as the ratio of the partial pressure of water to its saturation vapor pressure at the same temperature. McRae suggested the following expression for the saturation vapor pressure [3]:

$$PH_2O\,(T) = Ps \exp\,(13.3185a - 1.9760a^2 - 0.6445a^3 - 0.12299a^4) \quad (7)$$

where, Ps is the standard atmospheric pressure
a is function of ambient temperature, T and steam temperature, TS;
a = 1-(Ts/T).

If the relative humidity (RH) is known, water vapor concentration in ppm and molality of absorbed species (m_i) can be found from the following relations:

$$(H_2O) = 10^4\,RH\,\frac{P^O_{H_2O}}{P} \quad (8)$$

$$m_i = \frac{1000}{18n_i}\;\frac{(1\text{-}RH)}{RH} \quad (9)$$

where n_i is number of moles of the absorbed species.

It is more convenient to express the atmospheric water content in term of a dimensionless volume fraction, L(volume of liquid water per volume of air). Typical L values for clouds are $10^{-7} - 10^{-6}$, Fogs are $5\times10^{-8} - 5\times10^{-7}$ and aerosols are $10^{-11} - 10^{-10}$

Gas/Aqueous Phases Equalibria

The equilibrium of a gaseous species A in water is usually given by Henry's Law:

$$[A\ (aq)\ ] = H_A\, P_A \tag{10}$$

where [A (aq)] is concentration of A in liquid (aqueous) phase.

H_A is Henry's law coefficient of A
P_A is partial pressure of A.

The distribution of species A in the gas and aqueous phases (D) can be known from the ratio of concentration of A in these phases for a certain volume of Air. This ratio is given by:

$$D = \frac{H_A\, P_A\, L}{P_A\, /RT} = H_A\, RTL \tag{11}$$

where R = Gas constanst.
T = Ambient temperature, °K.
L = Liquid water volume ratio, (M^3 water/M^3 air).

So for species A to be in the aqueous phase H_A, RTL must be greater than 1, or $H_A \gg (RTL)^{-1}$. In water cloud, $(RTL)^{-1} = 4 \times 10^4$ M atm^{-1}. Then if $H_A \ll 4 \times 10^4$ M atm^{-1}, species A will be present in the gas phase. Table 1 below shows Henry's law coefficient for NO, NO_2 and SO_2. They are much less than 4×10^4 M atm^{-1}. Actually, NO_x and SO_2 participate in additional aqueous phase dissociation equilibria.

Table 1. Coefficients of Henry's law

Gas	H_A, M atm^{-1} at 298°K
O_2	1.3×10^{-3}
NO	1.9×10^{-3}
O_3	9.4×10^{-3}
NO_2	1.0×10^{-2}
CO_2	3.4×10^{-2}
SO_2	1.24
HNO_2	49.0
H_2O_2	7.1×10^{-4}
HNO_3	2.1×10^{-5}

NO and NO_2 when absorbed by the atmospheric water form nitrite (NO_2^-) and nitrate (NO_3) ions according to the following reactions:

$$2NO_2 + H_2O \longrightarrow 2H^+ + NO_2^- \; ; K_{298} = 2.44 \times 10^2 \, M^4 . \, atm^{-2} \qquad (12)$$

$$NO + NO_2\,(g) + H_2O \longrightarrow 2H^+ + 2NO_2^- \; ; K_{298} = 3.2 \times 10^{-5} \, M^4 . \, atm^{-2} \qquad (13)$$

where K_{298} is the reaction rate constant at 298°K.

At 298°K, the ratio of nitrate to nitrite ions at equilibrium is:

$$\frac{(NO_3^-)}{(NO_2^-)} = 7.4 \times 10^6 \frac{P_{NO_2}}{P_{NO}} \qquad (14)$$

The nitrate ion is then the predominantly dissolved ion. From the equilibrium constants of the previous reactions, the dissolved nitric acid concentration is given by:

$$(HNO_3) \simeq (NO_3^-) = 206.4 \, (P_{NO_2}^3 / P_{NO})^{1/4} \qquad (15)$$

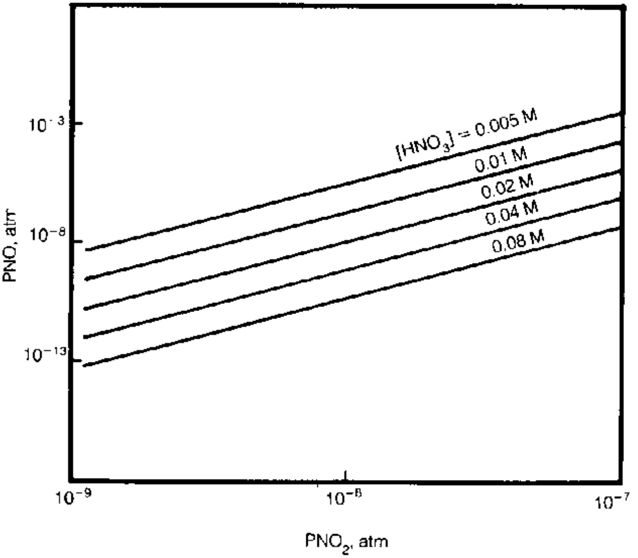


Fig. 3. Equilibrium concentration of nitric acid as a function of NO and NO_2 partial pressure.

Fig. 3 shows the variation of nitric acid concentration as function of NO_2 and NO partial pressure. This shows the importance of NO_2 in the removal of NO_x from the atmosphere. However, large amounts of NO can be emitted from various combustion sources. Conversion of NO into NO_2 takes place in the presence of sun light and ozone, hydrogen peroxides, and other radicals. Once NO_2 is formed, a series of complex photochemical reactions will be started exhausting most of the NO_2 concentrations. The formation of nitric acid rain may be formed by absorption of active species of nitrogen rather than direct absorption of NO and NO_2. Considerable amounts of the acid are formed in the gas phase and rapidly absorbed by water droplets due to its high absorption coefficient, see Table 1.

Absorption of SO_2 in water takes place according to the following reactions:

$$SO_2(g) + H_2O \longrightarrow H_2SO_3\,(aq)\;;\; K_1 = \frac{(H_2SO_3)}{P_{SO_2}} \tag{16}$$

$$H_2SO_3(aq) \longrightarrow H^+ + HSO_3^- \;;\; K_2 = \frac{(H^+)\,(HSO_3^-)}{(H_2SO_3)} \tag{17}$$

$$HSO_3 \longrightarrow H^+ + SO_3^{2-} \;;\; K_3 = \frac{(H^+)\,(SO_3^2)}{(HSO_3)} \tag{18}$$

where K_1, K_2 & K_3 are the reaction rate constants.

The total dissolved sulphur is given by

$$(S) = (SO_2\,(aq) + HSO_3^-) + (SO_3^{2-})$$

By substitution for each concentration from the equilibrium reactions:

$$(S) = K_1\, P_{SO_2} \left(1 + \frac{K_2}{(H^+)} + \frac{K_2\, K_3}{(H^+)^2} \right) \tag{19}$$

It is evident that the amount of sulphur dissolved depends on the pH value. Maahs recommended the following values for the equilibrium constants [4; p. 187]:

$$\text{Log}\, K_1 = \frac{1376.1}{T} - 4.521 \tag{20}$$

$$\text{Log } K_2 = \frac{853}{T} - 4.74 \tag{21}$$

$$\text{Log } K_3 = \frac{621.9}{T} - 9.278 \tag{22}$$

where K has the practical unit M and T is in K.

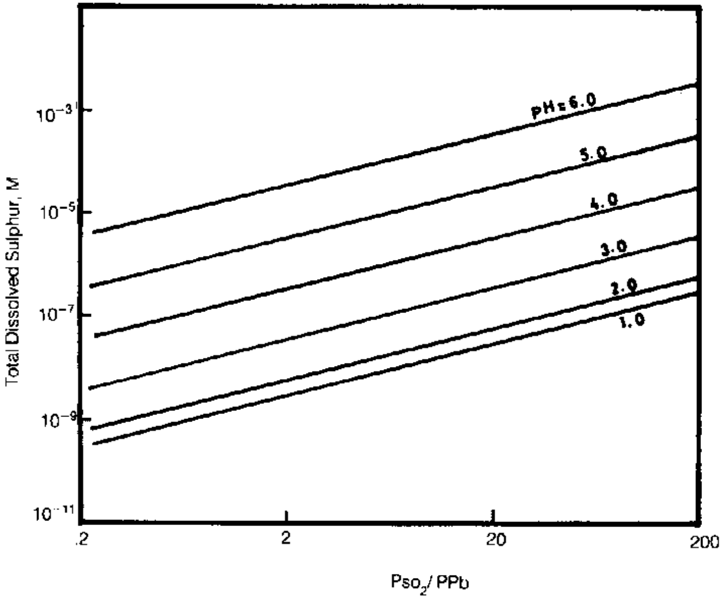


Fig. 4. **Equilibrium concentration of dissolved sulphur vs SO_2 partial pressure at 298° K and different pH values.**

In Fig. 4, generated from equations (19) to (22), the total dissolved sulphur concentration is plotted *vs* SO_2 partial pressure at different pH values. Aqueous phase absorption of SO_2 is the major removal process of this gas from the atompshere. Oxidation of SO_2 may take place in the gas phase according to the following reaction:

$$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3 \, ; \, K_{298} = 2.6 \times 10^{12} \tag{23}$$

At an oxygen partial pressure of 0.2 atm (the average atmospheric value), the ratio of partial pressure of SO_3 to SO_2 is about 1.19×10^{12}. This indicates that the SO_3 or S (VI) state is the thermodynamically preferred state of sulphur oxide at ambient temperature. Equal SO_3 and SO_2 vapor pressures occur at 711°C.

Also a very small concentration of SO_2 would remain in the atmosphere. Consider the following reaction,

$$SO_2\,(g) + \frac{1}{2}\,O_2\,(g) + H_2O \xrightarrow{\qquad} H_2SO_4\,(aq)\;;\; K_{298} = 6.23 \times 10^{37} \tag{24}$$

at typical ambient concentration of oxygen and moisture, the partial pressure of SO_2 will be in the order of 3×10^{-36} atm. So traces of SO_2 may be present unattached in a wet atmosphere.

When SO_2 dissolves in water three sulphur-containing species are formed. First H_2SO_3 or SOH_2O is formed which then ionizes to bisulfite, HSO_3^-, and sulfite, SO_3^{-2}, ions. Sulfate ions, SO_4^{-2}, are eventually formed. This is referred to as S(VI). Other atmospheric species such as hydrogen peroxide, H_2O_2, ozone, nitrogen containing species and metal ions oxidize SO_2 in the aqueous phase. Table 2 lists the rate expression for each oxidant. A comparison between the SO_2 oxidation rate by these species are presented in Fig. 5 [5].

At pH less than 5, SO_2 oxidation by H_2O_2 is predominant. For pH values near 5 or greater, O_3 oxidation is important. Uncertainties in the rate of Fe and Mm oxidation weaken the importance of these species for SO_2 oxidation at high pH values [5]. SO_2 oxidation by NO_2 and HNO_2 are unimportant within the pH range of interest.

Hydrogen peroxide is formed in the atmosphere by decomposition of HO_2 ions according to the following reactions,

$$2HO_2 \xrightarrow{\qquad} H_2O_2 + O_2$$

$$HO_2 + H_2O \xrightarrow{\qquad} H_2O\,HO_2$$

$$H_2O\,HO_2 + HO_2 \xrightarrow{\qquad} H_2O_2 + H_2O + O_2$$

HO_2ions may undergo a large number of reactions in the atmosphere reducing the probability of H_2O_2 formation. Also H_2O_2may be photodissociated by light of wavelength ranging from 0.2 to 0.35 um. Table 3 shows the aqueous fractions of H_2O_2 and O_3 at different atmospheric moisture content [5], as a function of water ratio in the air.

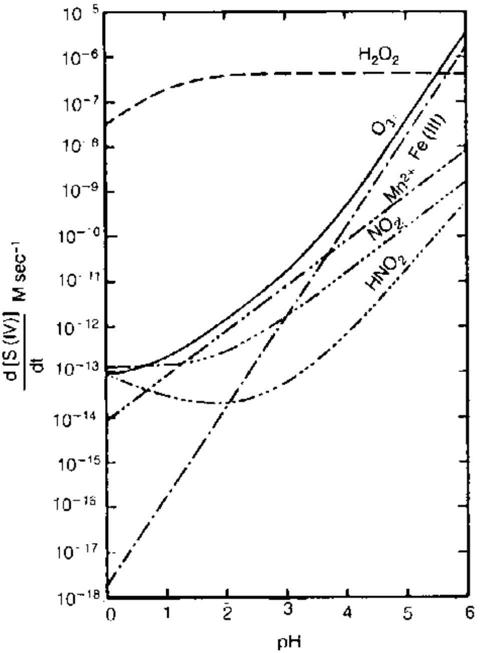
Table 2. Rate expression for sulfate formation in aqueous solution [5]

Oxidant	Rate expression, $-\dfrac{d[S(IV)]}{dt}$
O_3	$(k_0[SO_2H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3(aq)]$ $k_0 = 2.4 \times 10^4\ M^{-1}\ sec^{-1}$ at 298°K $k_1 = 3.7 \times 10^5\ M^{-1}\ sec^{-1}$ $k_2 = 1.5 \times 10^9\ M^{-1}\ sec^{-1}$
H_2O_2	$\dfrac{k[H^+][HSO_3^-][H_2O_2(aq)]}{1 + [KH^+]}$ $k = 7.45 \times 10^7\ M^{-1}\ sec^{-1}$ at 298°K $k = 13\ M^{-1}$
Fe (III)	$k[Fe(III)][SO_3^{2-}]$ $k = 1.2 \times 10^6\ M^{-1}\ sec^{-1}$ at 293 $pH \leq 5$
Mn (II)	$k_2[Mn(II)][HSO^-{}_3]$ $k_2 = 3.4 \times 10^3\ M^{-1}\ sec^{-1}$ at 298°K $[S(IV)] \leq 10^{-4}\ M$ $[Mn(II) \leq 10^{-5}\ M$ $k_1[Mn^{2+}][H^+]^{-1}\beta_1$ $k_1 = 2 \times 10^9\ M^{-1}\ sec^{-1}$ $\beta_1 = \dfrac{[Mn_2OH^{3+}][H^+]}{[Mn^{2-}]}$ $\beta_1 = 10^{-9.9}$ at 298°K
N(III)[a]	$k[H^+]^{1/2} H_{HNO_2} H^*_{S(IV)} P_{HNO_3} P_{SO_2} \left(1 + \dfrac{K_{n4}}{[H^+]}\right)$ $k = 142\ M^{-3/2}\ sec^{-1}$ at 298°K
NO_2	$kH_{NO_2} H^*_{S(IV)} P_{NO_2} P_{SO_2}$ $k = 2 \times 10^6\ M^{-1}\ sec^{-1}$ at 298°K

a$[N(III)] = [HNO_2(aq)] + [NO_2^-]$ where

$HNO_2(g)$ $HNO_2(aq)\ H_{HNO_2}$
$HNO_2(aq)$ $H^+ + NO_2^-\ K_{n4}$
$[N(III)] = H_{NO_2}\ PHNO_2[1 + K_{n4}/[H^+]]$

H^*_S (IV): Henery constant for Sulfur (IV).



$[HNO_2(g)] = 2$ ppb; $[H_2O_2(g)] = 1$ ppb; $[NO_2(g)] = 1$ ppb; $[O_3(g)] = 50$ ppb;

$[Fe^{3+}(aq)] = 3 \times 10^{-7}$ M; $[Mn^{2+}(aq)] = 3 \times 10^{-8}$ M, $[SO_2(g)] = 5$ ppb

Fig. 5. Oxidation rates of SO_2 in west atmosphere by different oxidations [5].

Table 3. Mass fraction of H_2O_2 and O_3 in wet atmosphere [5]

L (m^3 water/m^3 air)	H_2O_2	O_3
10^{-5}	0.95	2.3×10^{-6}
10^{-6}	0.63	2.3×10^{-7}
10^{-7}	0.15	2.3×10^{-8}

Conclusions

The formation and precipitation of nitric and sulphuric acids depend on pH, water content of atmosphere and concentrations of NO_x and SO_2. Nitrogen oxides participate in complex gas phase reactions, so called photochemical reactions. Nitric acid is most probably absorbed into the atmospheric water droplets as soon as it forms in the gas phase. On the other hand most of the SO_2 conversion reactions occur in the aqueous phase.

Possible mechanisms and rates of oxidation of NO_x and SO_2 in gas and aqueous phases are discussed. The rate of oxidation of So_2 in a wet atmosphere depends in the presence of H_2O_2 and/or O_3 and on pH.

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إزالة الغازات الملوّثة في الأجواء الرطبة

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ملخص البحث. تتأكسد الغازات الملوّثة مثل ثاني أكسيد الكبريت وأكاسيد النيتروجين حال انبعاثها إلى سلفات نترات خلال بعض الطرق الغازية والمائية. ويُعَدّ امتصاص الغازات الملوّثة على قطرات الماء البداية الأساسية لعملية إزالة هذه الغازات من الهواء. وتحتوي عملية الامتصاص هذه على خطوات معقدة تشمل الإذابة والامتصاص داخل وخارج قطرات الماء.

ويناقش هذا البحث الخطوات الممكنة للامتصاص كمثال لسلوك الملوّثات الغازية في الهواء الجوي، وعلى الرغم من أن المملكة العربية السعودية ذات جو جاف إلا أن هذه الظاهرة مهمة في المناطق الساحلية من البلاد خاصة في فصل الصيف.