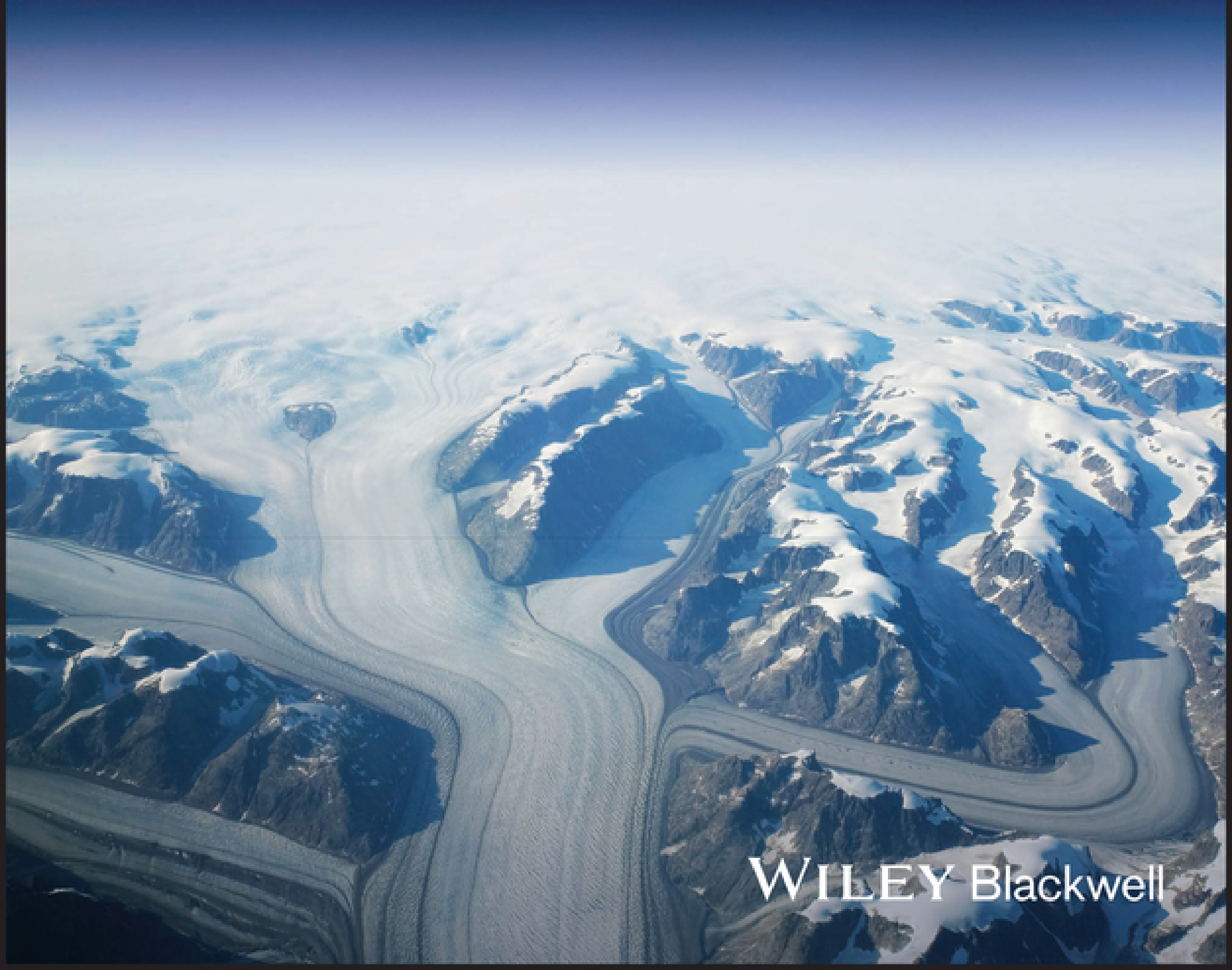
HAJIME AKIMOTO | JUN HIROKAWA

ATMOSPHERIC MULTIPHASE CHEMISTRY

FUNDAMENTALS OF SECONDARY AEROSOL FORMATION



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Atmospheric Multiphase Chemistry

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Fundamentals of Secondary Aerosol Formation

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Preface

Reaction kinetics and mechanism are a significant part of the fundamentals of atmospheric chemistry. The chemical reaction system in the atmosphere is composed of homogeneous reactions in the gas and liquid phases and heterogeneous processes involving particle surfaces. Among them, the study of gas-phase homogeneous reaction system in the atmosphere has evolved since the Chapman theory in the 1930s to explain the stratospheric ozone layer, and developed dramatically after 1970s with photochemical air pollution as a trigger. It is now almost established and summarized in many bibliographies, including a book by one of present authors (H.A.) discussed in Chapter 3.

In contrast, although the heterogeneous reaction system in the atmosphere has developed substantially with acid rain and stratospheric ozone hole as turning points, the studies have long been confined mainly to inorganic species. The research field of aerosols and heterogeneous kinetics has undergone dramatic changes since the 2000s, when the importance of secondary organic aerosols as cloud condensation nuclei was pointed out. Also, secondary organic aerosols have been recognized as important as inorganic sulfate and nitrate as a constituent of $PM_{2.5}$, which is concerned from the point of human health.

The formation mechanism of secondary organic aerosols involves condensation of reaction products of homogeneous gas-phase reactions, uptake of the gas-phase products onto the particle surface, complex formation and reaction at the interface, homogeneous aqueous-phase reaction, and evaporation from a particle to the gas phase. We call series of these processes multiphase reaction chemistry.

This book intends to serve as a reference book on fundamentals of atmospheric multiphase chemistry. Gas- and aqueous-phase reactions, heterogeneous oxidation processes, and air–water interface and solid particle surface reactions related to secondary organic aerosol formation are first described. After that, new particle formation, cloud condensation nucleus activity, and field observation of organic aerosols are discussed. The book can serve as a comprehensive reference for graduate students and professionals who are interested in homogeneous and heterogeneous atmospheric reactions of organic species related to aerosols.

The field of atmospheric multiphase chemistry is still a rapidly developing research area. Many studies described in this book have not become fully established, and future revisions are likely.

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October, 2019

Hajime Akimoto
Jun Hirokawa

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Historical Background of Atmospheric Secondary Aerosol Research

1.1 Introduction

Trace components in the tropospheric atmosphere consist of gaseous molecules and particulate matters. Most of gaseous molecules in the atmosphere do not have absorption bands in the visible region. Some species such as ozone and nitrogen dioxide have the absorption, but they are invisible to the naked eye under the normal atmospheric conditions because their absorbance are small. In contrast, since the particulate matters intercept sunlight and small particles scatter strongly the solar radiation, they are captured easily by the naked eye as haze. Thus, particulate matters in the atmosphere called atmospheric aerosols have been studied from relatively early days in relation to air pollution historically.

These atmospheric aerosols are divided broadly into the primary species released directly from emission sources and the secondary compounds formed by chemical reactions in the atmosphere. Further, secondary particulate matter can be classified into secondary inorganic aerosol and secondary organic aerosol (SOA).

This book aims at the understanding of chemical reactions forming secondary aerosols in the gas phase, in the liquid phase, and at their interface, particularly focusing on organic aerosols. Therefore, most of the descriptions are focused on organic species, and inorganic species are addressed whenever necessary. As for the formation of secondary inorganic aerosols, detailed discussion has been given by the textbook of Seinfeld and Pandis (2016).

In this chapter, historical background of research on atmospheric secondary aerosols, including inorganic aerosols, is described looking back before 1980s, when the atmospheric chemistry was founded as one of the academic fields of the global environmental sciences.

1.2 Secondary Inorganic Aerosols

The first capture of atmospheric secondary inorganic aerosol such as nitrate and sulphate was in the form of precipitation component, and their historical reviews are available by Eriksson (1952a, 1952b) and Möller (2008). First discovery of nitrate in precipitation was made by Marggraf (1751), a German chemist, and mineral species (silica and lime), sea salt component (sodium and chloride), ammonium, and organics as brown residue were also detected together with nitrate. It was the earlier half of

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nineteenth century when Liebig (1835) advocated a theory that atmospheric nitrogen compounds deposited on ground are essential to plant growth as nutrient salt absorbed by roots, leading to a revolution of agricultural chemistry. Thus, atmospheric nitrate, the main component of the plant nutrient, had been discovered from long ago as a precipitation constituent (Miller 1905; Eriksson 1952a; Möller 2008). On the other hand, the discovery of sulphate was delayed nearly 100 years after that of nitrate. From the view point of air pollution in Manchester, UK, Smith (1852) described based on the analysis of precipitation that three kinds of air can be found: (i) with carbonate of ammonia in the remote field; (ii) with sulphate of ammonia in the suburbs; and (iii) with sulfuric acid in the urban area (Cowling 1982). The described ammonium carbonate ($(NH_4)_2CO_3$), ammonium sulfate ($(NH_4)_2SO_4$), and sulfuric acid (H_2SO_4) are formed secondarily by the chemical reactions in the gas phase or in the fog water from atmospheric trace gaseous species, CO_2, NH_3, and SO_2. These aerosols are water-soluble, and recognized as major components of "acid rain" after taken into precipitation. Incidentally, the term of *acid rain* was used for the first time in the monograph of Smith (1872) as accredited by Cowling (1982). Since then, the measurement of nitrate and ammonium had been made in many places in Europe in the latter half of nineteenth century from the interest of agricultural chemistry, while sulfate had been measured in the eastern part of United States since the 1910s (Cowling 1982).

Hydrogen ion concentration (pH) has been measured since the 1950s, started in Europe and United States, over a wide area. Owing to these wide-area observations, spatial distribution and temporal trends of pH and chemical components of precipitation became to be known well in Europe (Emanuelsson et al. 1954; Barrett and Brodin 1955; Odén 1976) and North America (Junge and Werby 1958; Gorham and Gordon 1960; Cogbill 1976). The acid rain causing acidification of lakes and rivers and their impact on fishery was then brought up as a social problem internationally. The quantitative research on the formation of sulfate and nitrate as secondary inorganic aerosol had been developed rapidly as "acid rain" became social concern.

1.2.1 Sulfate

In the earlier studies on acid rain, it was thought that sulfur dioxide (SO_2), primary air pollutants whose atmospheric concentration had increased rapidly after the Industrial Revolution, was taken up into fog water droplets and converted to sulfate by oxidation in the aqueous phase (Junge and Ryan 1958; Junge 1963):

$$SO_2 \xrightarrow{H_2O} SO_3{}^{2-} \xrightarrow[M^{n+}]{O_2} SO_4{}^{2-} \xrightarrow{NH_4{}^+} (NH_4)_2SO_4 \tag{1.1}$$

The rate limiting stage of this process is the oxidation step of $SO_3{}^{2-}$ to $SO_4{}^{2-}$, and the oxidation by O_2 had been studied for a long time (Fudakowski 1873; Backstrom 1934). However, the oxidation rate of $SO_3{}^{2-}$ by O_2 was found to be very slow (Fuller and Crist 1941; Brimblecombe and Spedding 1974). Therefore, this reaction is not important for O_2 alone as the oxidation reaction of SO_2 in the atmosphere, but it was found that the reaction is accelerated by the coexistence of trace metal ions such as Fe^{3+}, Cu^{2+}, and Mn^{2+} (Reinders and Vles 1925; Junge and Ryan 1958; Brimblecombe and Spedding 1974; Hegg and Hobbs 1978). The effects of transition metal ions on the SO_2 oxidation in the aqueous phase still leaves a lot of unknowns, and the studies are ongoing (Deguillaume et al. 2005; Harris et al. 2013; Herrmann et al. 2015).

In 1970s, the importance of the reaction of O_3 and H_2O_2, formed secondarily in the photochemically polluted atmosphere, was pointed out. The pioneering studies were made by Penkett and Garland (1974), Erickson et al. (1977), and Larson et al. (1978) for O_3, and by Mader (1958), Hoffmann and Edwards (1975), and Penkett et al. (1979) for H_2O_2. Later studies on these aqueous phase reactions revealed that the oxidation by H_2O_2 is more important at lower pH than 7, and those of O_3 become important in the higher pH region. Details of these aqueous-phase reactions are summarized in the textbooks by Akimoto (2016, pp. 363–372), and Seinfeld and Pandis (2016).

Atmospheric oxidation reactions of SO_2 to SO_4^{2-} were studied earlier for the aqueous-phase reactions, and the gas-phase reactions was noted later by Cox and Penkett (1972). The years of 1970s are the era that OH radical chain reactions were proposed and demonstrated to cause photochemical air pollution (Akimoto 2016, pp. 288–290). The importance of the reaction of SO_2 and OH for the oxidation of SO_2 was deduced based on the measured rate constant of the reaction (Eggleton and Cox 1978; Davis et al. 1979). Later, Stockwell and Calvert (1983) showed the oxidation process of SO_2 with OH as

$$OH + SO_2 + M \rightarrow HOSO_2 + M \tag{1.2}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{1.3}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \tag{1.4}$$

$$HO_2 + NO \rightarrow NO_2 + OH \tag{1.5}$$

This implies that the $HOSO_2$ forms H_2SO_4 without terminating the OH chain reaction. The SO_2 oxidation mechanism in the gas-phase has thus been established. Although the relative importance of gas- and aqueous-phase reactions varies widely, depending on meteorological conditions. It is thought in general that both processes are important (Barrie et al. 2001). Most of sulfate in particles exist as ammonium sulfate ($(NH_4)_2SO_4$) or ammonium bisulfate (NH_4HSO_4), and a part of them exists as sulfuric acid (H_2SO_4) when NH_3 is in short stoichiometrically as observed in the sub-micron particles in many urban samples (van den Heuvel and Mason 1963; Ludwig and Robinson 1965; Wagman, Lee, and Axt 1967).

1.2.2 Nitrate

The measurement of nitrate (NO_3^-) in precipitation has been reported in United States early in 1920s from the interest in agricultural chemistry (Wilson 1926). Its atmospheric concentrations increased rapidly, accompanying with the rapid increase of fossil fuel combustion. It has been monitored since the 1950s as an important secondary inorganic aerosol next to SO_4^{2-} (Junge 1954; Lee and Patterson 1969). For example, the equivalent-basis fractions of SO_4^{2-} and NO_3^- in precipitation in Eastern United States in early 1960s are reported as ca. 60% and ca. 20%, respectively (Likens and Bormann 1974). Particularly, large amounts of nitrates were reported, together with sulfate and organic aerosols existing in photochemical smog mentioned in the next section (Renzetti and Doyle 1959; Lundgren 1970; Appel et al. 1978).

Since the rate constant of the reaction:

$$OH + NO_2 + M \rightarrow HNO_3 + M, \tag{1.6}$$

is one order of magnitude larger than the reaction, $OH + SO_2 + M$, under the atmospheric conditions, and the Henry's law constant of NO_2 is two orders of magnitude smaller than SO_2 (Table 2.2), nitric acid (HNO_3) in the atmosphere is thought to be formed in the gas phase and then taken into the aqueous phase (Orel and Seinfeld 1977). Meanwhile, a formation pathway other than (1.6) is considered to be the hydrolysis of N_2O_5 formed via NO_3 by the reaction of O_3 and NO_2 (Orel and Seinfeld 1977):

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1.7}$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \tag{1.8}$$

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3 \tag{1.9}$$

The rate constant of Reaction (1.9) in the gas phase as a homogeneous reaction is very small, $<2.0 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (Burkholder et al. 2015), and the heterogeneous reaction on the particle surface is thought to be more important (Mozurkewich and Calvert 1988). The NO_3 radical involved in this reaction process has absorption bands in the visible region and photolysed easily by sunlight, so that the formation of HNO_3 by this heterogeneous reaction process is thought to be important in the nighttime (Richards 1983; Heikes and Thompson 1983).

The gaseous nitric acid, ammonia, and ammonium nitrate formed from them are thought to be in equilibrium:

$$NH_3(g) + HNO_3(g) \leftrightarrows NH_4NO_3(s), \tag{1.10}$$

and comparison between model estimate based on the thermodynamic parameters (Stelson et al. 1979) and field observation for the formation of nitrate have been made (Harrison and Pio 1983; Hildemann et al. 1984). Reaction (1.10) is reversible reaction, and the particulate NH_4NO_3 increases with the decrease of temperature, and thus the concentration ratio of nitrate is known to increase in winter and at dawn. Multiphase models that treat sulfuric and nitric acid simultaneously have been developed in 1980s (Bassett and Seinfeld 1983; Saxena et al. 1983).

Gaseous HNO_3 reacts with sea salt (NaCl) on the surface to give sodium nitrate by releasing HCl:

$$NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g). \tag{1.11}$$

Although it has been presumed that the reaction causes the decrease of chlorine to sodium ratio in the sea salt in the vicinity of continents and brings the nitrate in coarse particles (Robbins et al. 1959), the reaction has been validated by laboratory experiments only after the latter half of 1990s (De Haan and Finlayson-Pitts 1997; Wahner et al. 1998). Thus, nitrates have the characteristics that they exist as NH_4NO_3 in submicron particles in the inland and as $NaNO_3$ in coarse particles (2–8 μm) in the coastal urban area (Lee and Patterson 1969; Cronn et al. 1977).

1.3 Secondary Organic Aerosols

Existence of organic materials in the precipitation was noted by Marggraf (1751) in the middle of eighteenth century, and they were more clearly identified as humic acid-like substances in the first half of the nineteenth century (Lampadius 1837; Möller 2008).

However, the trigger to wide concern on the particulate organic compounds was the discovery of carcinogenic polyaromatic hydrocarbons (PAHs) in the diesel exhaust and urban atmosphere in the middle of twentieth century (e.g. Waller 1952; Kotin et al. 1954; Stocks and Campbell 1955; Wynder and Hoffmann 1965). Further findings of many oxygenated compounds in the atmospheric aerosols were made in the photochemical smog.

1.3.1 Photochemical Smog

In the middle of the 1940s, new type of smog totally different from conventional air pollution due to SO_2, sulfate, and coal fly ash, spread in Los Angeles basin, and became a social problem by causing visibility reduction, eye and throat irritation, and particularly big damage to agriculture (Middleton et al. 1950; Finlayson-Pitts and Pitts 2000). Although the cause of so-named Los Angeles smog was unexplained at the beginning, Haagen-Smit (1952), and Haagen-Smit, Bradley and Fox (1956) elucidated for the first time that it is ascribed to the toxic substances, including ozone and other strongly oxidizing compounds so-named *photochemical oxidants,* formed by the solar irradiation to the mixtures of nitrogen oxides and non-methane hydrocarbons (NMHCs) emitted from automobile exhaust. Such atmospheric photochemical processes were systematized by Leighton (1961), and his book, *Photochemistry of Air Pollution* is now a classic of atmospheric photochemistry. Los Angeles smog was later called *photochemical smog* (e.g. Rogers 1958), and the term, *photochemical air pollution*, is now widely used including more general concept (e.g. Robinson 1972).

In photochemical smog, other than gaseous oxidants, many kinds of organic aerosols together with sulfate and nitrate were found as particulate matter, and these were shown to be SOAs, formed by the photo-irradiation of the mixtures of NO_x and NMHCs such as auto exhaust (Mader et al. 1952; Renzetti and Doyle 1959). Incidentally, the NMHC was used as a general term for the collectives of short-lived hydrocarbons, excluding methane, which has a longer atmospheric lifetime of nearly 10 years and does not contribute to urban photochemical air pollution directly. Recently, instead of NMHC, the term nonmethane volatile organic compounds (NMVOC) has been more widely used to include oxygen-containing organic compounds other than hydrocarbons. From the early days of the study on the formation mechanism of photochemical smog, there was interest in what kinds of hydrocarbons generate SOAs more effectively. Studies of Haagen-Smit (1952) showed that cyclic hydrocarbons with double bonds such as cyclohexene, indene, and cyclopentadiene easily form low-volatile oxygenated compounds with higher yields of aerosols, since the multiple functional groups are introduced by the ring-opening reactions. This was later confirmed by O'Brien, Holmes, and Bokian (1975), and they reported α-pinene having a cyclic double bond and dialkenes such as isoprene form aerosols with the higher yields, and monocyclic aromatic hydrocarbons such as xylenes also form aerosols with the lower yields.

In the organic aerosols, particulate alkanes, alkenes, alkylbenzenes, naphthalene, etc. were detected as primary organic aerosols (POAs) released directly from emission sources, and pinonic acid, adipic acid, phenols, alkyl nitrates, etc. as SOA formed in the atmosphere. Primary aerosols are not correlated with ozone, but the secondary aerosols have a high correlation with ozone and have peak concentration in early afternoon. Such clear distinction between the POA and SOA was made in the middle of 1970s (Appel, Colodny, and Wesolowski 1976; Cronn et al. 1977). These early studies showed that alcohols, carboxylic acids, and carbonyl compounds are included in the aerosols by use of infrared absorption spectroscopy and mass spectrometry (Cukor et al. 1972; Ciaccio et al. 1974; Cronn et al. 1977). Also, it was revealed that atmospheric carbonaceous aerosol sampled in California consisted of elemental carbon (EC) and organic carbon (OC) (Appel, Colodny and Wesolowski 1976).

1.3.2 Blue Haze

It is experienced for a long time that the atmosphere in the boundary layer over forests is covered by blue haze after the air is cleaned by rain in summer. In 1950s, a botanist, Went (1960a) addressed the interest to this phenomenon from the viewpoint of atmospheric aerosols. In the "Blue Mountains" near Sydney, Australia, and "Blue Ridges" near the Smoky Mountains in Tennessee, United States, such blue haze are often visible (Ferman, Wolff, and Kelly 1981). Went (1960a) mentioned that a similar phenomenon in Tuscany, Italy, was described in a note by Leonardo da Vinci a long time ago in sixteenth century. This kind of haze is not natural dust or mist, nor the effects of biomass burning or air pollution, and can be seen in dry air irrelevant to water vapor. From these considerations Went (1960a) concluded that blue haze is due to the Tyndall effect described by Tyndall (1869) in the middle of nineteenth century, a phenomenon that a light path can be seen bright from an oblique due to scatter of light by fine particles in air. He proposed that when the fine particles with a diameter of the order of 0.1 μm exist in the atmosphere, blue light in the solar light is effectively scattered and blue haze is visible.

As for the possibility of formation of such sub-micron fine particles over the clean forests, Went (1960b) suggested that the photochemical smog reaction of hydrocarbons such as terpenes and isoprene emitted by plants. However, atmospheric concentrations of such biogenic hydrocarbons were not known in early 1960s. They were measured for the first time by Rasmussen and Went (1965), and total concentration of isoprene and terpenes up to ~10 ppbv was reported in several forest highlands in United States.

Later measurement of chemical composition of field aerosols at Great Smoky Mountains showed that the main component of fine particles is sulfate and the fraction of organic compounds are relatively small (Stevens et al. 1980; Ferman, Wolff, and Kelly 1981) in those days. Seasonality of the aerosol components were shown that concentrations of sulfate and organic aerosols are high in summer and that of nitrate is high in winter, reflecting the photochemical formation of SO_4^{2-} and OA, and temperature-dependent gas-solid equilibrium of NH_4NO_3 (Day, Malm, and Kreidenweis 1997). Meanwhile, although the measurement of chemical analysis of aerosols in Blue Mountains in Australia is scarce, solvent extracted organics contains n-alkane, n-alkanoic acid, and n-alcohol, which compose lipids contained in plant wax (Simoneit et al. 1991).

It is interesting to note that the prototype of SOA formation from biogenic and anthropogenic hydrocarbons was thus shown in early studies more than 50 years ago. The research on SOA has been developed extensively after the year of 2000 being related to the interests in the impact on human health of $PM_{2.5}$ and in the climate impact of aerosols.

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2

Fundamentals of Multiphase Chemical Reactions

2.1 Introduction

Chemical reaction systems in the atmosphere are composed of homogeneous reactions in the gas phase, homogeneous liquid-phase reactions in deliquescent aerosol particles and water droplets, and heterogeneous reactions at the particle surface. Among them, physicochemical fundamentals of photochemistry and kinetics in the homogenous gas phase reactions have already been well established in principle, and detailed explanation has been given in a previous book by one of the present authors (Akimoto 2016) and many textbooks introduced therein. In contrast, many aspects of atmospheric multiphase chemical reactions, including uptake of chemical species from gas phase to particle surface, heterogeneous reactions at the surface, and homogeneous aqueous phase reactions, have not yet been well established. In this chapter, fundamentals of physical chemistry relevant to the formation and transformation of atmospheric aerosols are described. The values of physical constants appearing in this book and the conversion factors of energy units between kJ, kcal, and eV are given in Tables 2.1 and 2.2.

In this chapter, fundamentals of optical properties, such as scattering of light and photoabsorption by atmospheric fine particles, and the photochemistry related to the photolysis at the surface of fine particles are not covered. The former topics are covered by the textbook by Mishchenko et al. (2002) and Kokhanovsky (2008), but the systematic research on the latter topic has not been developed well and is still open to future research.

2.2 Gas–Liquid Phase Equilibrium and Equilibrium in Liquid Phase

In the gas–liquid phase equilibrium, the experimental discovery that the amount of gaseous molecules dissolving into the liquid phase is proportional to the partial pressure of the substance in the gas phase was made by a British chemist, William Henry (1803), and the proportional constant is called Henry's law constant after his name. The Henry's law constant is an important parameter in atmospheric chemistry, which describes the partitioning of trace chemical species between the air and the cloud/fog and aqueous aerosol particles. Before the specific discussion of Henry's law constant and ion dissociation, general treatment of thermodynamics of chemical equilibrium is described in this section as underlying bases.

Atmospheric Multiphase Chemistry: Fundamentals of Secondary Aerosol Formation,
First Edition. Hajime Akimoto and Jun Hirokawa.

Table 2.1 Physical constants.

Constants	Values
Boltzmann constant (k_B)	1.3807×10^{-23} J K^{-1}
Plank constant (h)	6.6261×10^{-34} J s
Light velocity (in vacuum) (c)	2.9979×10^{8} m s^{-1}
Avogadro constant (N_A)	6.0221×10^{23} mol^{-1}
Gas constant (R)	8.3145 J K^{-1} mol^{-1} = 0.082058 L atm K^{-1} mol^{-1}

Table 2.2 Energy conversion table.

	kJ mol^{-1}	kcal mol^{-1}	eV
kJ mol^{-1} =	1	×0.2390	×0.01036
kcal mol^{-1} =	×4.184	1	×0.04337
eV =	×96.49	×23.06	1

2.2.1 Fundamentals of Thermodynamics

2.2.1.1 Internal Energy and Enthalpy

If we represent the internal energy (the sum of kinetic and potential energy of atoms, molecules, and ions constituting the system) by U, the work done from the surroundings to the system by w, and the heat applied from the surroundings to the system by q, the changes of internal energy ΔU is expressed as

$$\Delta U = q + w \tag{2.1}$$

from the first law of thermodynamics. Putting the infinitesimal changes of U, w, and q as $\mathrm{d}U$, δw, and δq, we obtain

$$\mathrm{d}U = \delta q + \delta w \tag{2.2}$$

from Eq. (2.1). Here, considering only the work done by the change of volume V by $\mathrm{d}V$ against the external pressure p_{ext}, δw is expressed as

$$\delta w = -p_{\text{ext}}\,\mathrm{d}V. \tag{2.3}$$

For the reversible change, keeping the equilibrium between the system and the surroundings, the pressure of the system p is equal to the pressure of the surroundings p_{ext}, so that $p = p_{\text{ext}}$ and Eq. (2.3) can be rewritten by

$$\delta w_{\text{rev}} = -p\,\mathrm{d}V, \tag{2.4}$$

and Eq. (2.2) becomes

$$\mathrm{d}U = \delta q - p\mathrm{d}V. \tag{2.5}$$

For the constant volume change ($\mathrm{d}V = 0$),

$$\mathrm{d}U = \delta q, \tag{2.6}$$