MODELING ATMOSPHERIC CHEMISTRY: INTERACTIONS BETWEEN GAS-PHASE SPECIES AND LIQUID CLOUD/AEROSOL PARTICLES

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Abstract. For detailed modeling of atmospheric chemistry it is necessary to consider aqueous-phase reactions in cloud droplets and deliquesced aerosol particles. Often, the gas-phase concentration is in equilibrium with the aqueous phase. Then Henry's law can be used to describe the distribution between the phases provided that the Henry's law coefficient is known. In some cases, thermodynamic equilibrium will not be reached and it is necessary to use kinetic expressions of the rates involved. These rates depend on diffusion constants, accommodation coefficients, Henry's law coefficients, particle size distributions, and several other parameters. This review describes how these processes can be treated in computer modeling and how the necessary data can be obtained. Even though it is written primarily for use in modeling atmospheric chemistry, some parts will also be useful for waste water and pesticide control and in other areas where the distribution of chemicals between the aqueous and the gas phase is important.

Keywords: heterogeneous atmospheric chemistry, Henry's law, accommodation coefficient, cloud droplet, aerosol particle, solubility, volatility, diffusion

1. Introduction

Although the liquid phase occupies only a very small fraction of the total volume of air (about 0.0001 % in clouds), it is recognized that it plays an important role in atmospheric chemistry. Many examples have been reviewed by Graedel and Weschler (1981). For example, the in-cloud production of H_2SO_4 from its precursor SO_2 is much faster than the gas-phase reaction. Clouds also affect the photochemistry of O_3, HCHO, and nitrogen oxides (Lelieveld and Crutzen, 1991). Even deliquesced aerosol particles (which contain much less water than cloud droplets) must be considered for an accurate description of atmospheric chemistry (e.g., Sievering et al., 1991, Chameides and Stelson, 1992, Sander and Crutzen, 1996, Vogt et al., 1996). This review describes how these processes can be treated in computer modeling and how the necessary data can be obtained. Section 2 shows how Henry's law coefficients can be used to describe the equilibrium between the phases. In Section 3 the kinetics of non-equilibrium conditions are reviewed. Fi-

nally, Section 4 summarizes how different aerosol size distributions can be treated in models of atmospheric chemistry and how they affect mass transfer processes.

TABLE I List of Symbols

Symbol	Quantity	SI-unit
α	accommodation coefficient	dimensionless
α_a	aqueous-phase accommodation coefficient	dimensionless
γ	uptake coefficient	dimensionless
γ^∞	infinite dilution activity coefficient	dimensionless
γ_b	activity coefficient (based on b)	dimensionless
γ_c	activity coefficient (based on c)	dimensionless
γ_x	activity coefficient (based on x)	dimensionless
λ	mean free path of a gas phase molecule	m
λ_{Sa}	'linear extrapolation distance'	dimensionless
φ	fugacity coefficient	dimensionless
ϱ	density	kg/m^3
σ	deviation from median in lognormal distribution	dimensionless
A	area	m^2
$A(r)$	surface of aerosol particles smaller than r	m^2/m^3
A_{tot}	total surface of aerosol particles	m^2/m^3
A	parameter for T dependence of k_H	dimensionless
b	molality	mol/kg
B	parameter for T dependence of k_H	dimensionless
C	parameter for T dependence of k_H	dimensionless
c_a	aqueous-phase concentration	mol/m$^3_{aq}$
$\bar{c_a}$	mean aqueous-phase concentration	mol/m$^3_{aq}$
$c_{a,sat}$	saturated aqueous-phase concentration	mol/m$^3_{aq}$
$c_{a,surf}$	c_a at the surface of a droplet	mol/m$^3_{aq}$
$c_{a,surf}^{eq}$	$c_{a,surf}$ in equilibrium with the gas phase	mol/m$^3_{aq}$
c_g	gas-phase concentration	mol/m$^3_{air}$
$c_{g,\infty}$	background gas-phase concentration	mol/m$^3_{air}$
$c_{g,surf}$	c_g at the surface of a droplet	mol/m$^3_{air}$
$c_{g,surf}^{eq}$	$c_{g,surf}$ in equilibrium with the aqueous phase	mol/m$^3_{air}$
c_T	total concentration (gas + aqueous)	mol/m$^3_{air}$
D	parameter for T dependence of k_H	dimensionless
D_a	aqueous-phase diffusivity	m^2/s
D_g	gas-phase diffusivity	m^2/s
$\Delta_{f,a} G$	molar free enthalpy of formation (aqueous phase)	J/mol

TABLE I List of Symbols (continued)

Symbol	Quantity	SI-unit
$\Delta_{\mathrm{f,g}}G$	molar free enthalpy of formation (gas phase)	J/mol
$\Delta_{\mathrm{soln}}G$	molar free enthalpy of dissolution	J/mol
$\Delta_{\mathrm{soln}}H$	molar enthalpy of dissolution	J/mol
$\tilde{J}_{\mathrm{c}}$	gas-phase diffusion flow	mol/s
J_{c}	gas-phase diffusion flux	mol/(m^2 s)
J_{k}	net flux through phase boundary	mol/(m^2 s)
$J_{\mathrm{k}}^{\mathrm{in}}$	flux through phase boundary into droplet	mol/(m^2 s)
$J_{\mathrm{k}}^{\mathrm{out}}$	flux through phase boundary out of droplet	mol/(m^2 s)
J_{x}	flux along x-axis	mol/(m^2 s)
k_{a}	first-order aqueous-phase rate constant	s^{-1}
$k_{\mathrm{a}}^{\mathrm{eff}}$	effective first-order aqueous-phase rate constant	s^{-1}
k_{dg}	rate constant for gas-phase diffusion	s^{-1} m$^3_{\mathrm{air}}$ m$^{-3}_{\mathrm{aq}}$
k_{i}	rate constant for interfacial mass transport	s^{-1} m$^3_{\mathrm{air}}$ m$^{-3}_{\mathrm{aq}}$
k_{mt}	mass transfer coefficient	s^{-1} m$^3_{\mathrm{air}}$ m$^{-3}_{\mathrm{aq}}$
$\bar{k}_{\mathrm{mt}}$	mean mass transfer coefficient	s^{-1} m$^3_{\mathrm{air}}$ m$^{-3}_{\mathrm{aq}}$
$k_{\mathrm{mt}}^{\mathrm{FS}}$	mass transfer coefficient (similar to k_{mt})	s^{-1} m$^3_{\mathrm{air}}$ m$^{-3}_{\mathrm{aq}}$
K_{A}	acid constant	mol/m$^3_{\mathrm{aq}}$
K_{B}	base constant	mol/m$^3_{\mathrm{aq}}$
k_{H}	Henry's law coefficient	miscellaneous
k_{H}^{bp}	Henry's law coefficient	mol/(kg Pa)
k_{H}^{cc}	Henry's law coefficient	dimensionless
k_{H}^{cp}	Henry's law coefficient	mol/(m$^3_{\mathrm{aq}}$ Pa)
$k_{\mathrm{H}}^{\mathrm{eff}}$	effective Henry's law coefficient	miscellaneous
$k_{\mathrm{H,inv}}$	inverse Henry's law coefficient	miscellaneous
$k_{\mathrm{H,inv}}^{cc}$	inverse Henry's law coefficient	dimensionless
$k_{\mathrm{H,inv}}^{pc}$	inverse Henry's law coefficient	m$^3_{\mathrm{aq}}$ Pa/mol
$k_{\mathrm{H,inv}}^{px}$	inverse Henry's law coefficient	Pa
Kn	Knudsen number	dimensionless
L	volume fraction of liquid water in air	m$^3_{\mathrm{aq}}$/m$^3_{\mathrm{air}}$
	(='dimensionless liquid water content')	
M	molar mass	kg/mol
N_{a}	number of molecules in the aqueous phase	dimensionless
N_{g}	number of molecules in the gas phase	dimensionless
$N(r)$	number density of aerosol particles smaller than r	1/m^3
N_{tot}	total number density of aerosol particles	1/m^3
n	amount of substance	mol

TABLE I List of Symbols (continued)

Symbol	Quantity	SI-unit
p	partial pressure $= c_{\mathrm{g}} R T$	Pa
p^*	vapor pressure of a solute in pure form	Pa
q	$r\sqrt{k_{\mathrm{a}}/D_{\mathrm{a}}}$	dimensionless
Q	$\bar{c}_{\mathrm{a}}/c_{\mathrm{a,surf}}$	dimensionless
R	gas constant	8.314 J/(mol K)
R_A	median droplet radius (surface distribution)	m
R_N	median droplet radius (number distribution)	m
R_V	median droplet radius (volume distribution)	m
r	droplet radius	m
t	time	s
T	temperature	K
$\bar{v}$	mean molecular velocity	m/s
$\bar{v}_{\mathrm{a}}$	aqueous-phase mean molecular velocity	m/s
V	volume	m^3
$V(r)$	volume of aerosol particles smaller than r	m^3/m^3
x	molar mixing ratio in the aqueous phase	mol/mol
y	molar mixing ratio in the gas phase	mol/mol

In some cases, the official SI-unit is different from the commonly used unit!
The superscript $^{\ominus}$ refers to standard conditions ($T^{\ominus} = 298.15$ K).
Chemicals enclosed in square brackets are aqueous-phase concentrations of that species: [X] = c_{a}(X)

2. Equilibrium Considerations: Henry's Law

2.1. DEFINING THE HENRY'S LAW COEFFICIENT k_{H}

Since many species can be found in the gas phase as well as in cloud droplets and aerosol particles, it is necessary to understand the distribution between the phases. According to Henry's law (named after the English chemist William Henry) the equilibrium ratio between the abundances in the gas phase and in the aqueous phase is constant for a dilute solution. The Henry's law coefficient describes this ratio at infinite dilution. IUPAC recommends k_{H} as the symbol for the Henry's law coefficient (Mills et al., 1993). However, other symbols like H and K_{H} are also frequently used. Here, k_{H} will be used as the symbol for the Henry's law coefficient in general (excluding the inverse Henry's law coefficients, see below). Different

superscripts will denote specific forms of k_H. There are numerous definitions and only those most frequently used can be presented here. See Tables II, III, and IV for conversion factors at standard conditions. If k_H refers to standard conditions ($T^{\ominus} = 298.15$ K) it will be denoted as $k_H^{\ominus}$.

Usually, the aqueous-phase composition is in the numerator and the gas-phase composition in the denominator of the definition of the Henry's law coefficient. Henry's law coefficients defined this way represent solubilities. Sometimes an inverse definition is used, representing the volatility instead. The generic symbol $k_{H,inv}$ will be used for these inverse coefficients. Since both k_H and $k_{H,inv}$ are frequently used, expressions such as 'a large Henry's law coefficient' are ambiguous unless it is explicitly stated whether the Henry's law coefficient is defined as a volatility or solubility.

Note that it is not possible to use the molar mixing ratio to describe the gas-phase composition. At a given gas-phase mixing ratio y, the aqueous-phase concentration c_a varies with the total pressure and the ratio y/c_a is not a constant value.

Some approximate values of Henry's law coefficients are shown in Figure 1. They cover many orders of magnitude. If an air parcel (e.g., cloud, fog, aerosol) is in equilibrium, N_g molecules will be in the gas phase, and N_a in the aqueous phase. To calculate which fraction $N_a/(N_g + N_a)$ of a species resides in the aqueous phase it is also necessary to know the liquid water content L. Figure 2 illustrates this for typical tropospheric values. Only a few species (such as HNO_3, HCl, and HBr) reside predominantly in the aqueous phase. However, many species are sufficiently soluble to significantly influence aqueous-phase chemistry.

2.1.1. Henry's Law Coefficient Defined via Concentration (k_H^{cp})

Atmospheric chemists often define the Henry's law coefficient as:

$$k_H^{cp} \overset{\text{def}}{=} \lim_{c,p \to 0} c_a/p. \tag{1}$$

Here, c_a is the concentration of a species in the aqueous phase and p is the partial pressure of that species in the gas phase under equilibrium conditions.

The SI unit for k_H^{cp} is $mol/(m_{aq}^3\, Pa)$. However, often the unit M/atm is used since c_a is usually expressed in M (1 M = 1 mol/dm^3) and p in atm (1 atm = 101325 Pa).

2.1.2. The Dimensionless Henry's Law Coefficient k_H^{cc}

Henry's law coefficient can also be expressed as the dimensionless ratio between the aqueous-phase concentration c_a of a species and its gas-phase concentration c_g:

$$k_H^{cc} \overset{\text{def}}{=} \lim_{c,c \to 0} c_a/c_g = k_H^{cp} \times RT \tag{2}$$

where R = gas constant and T = temperature.

TABLE II

Conversion factors between several Henry's law coefficients k_H representing solubility (at $T^\ominus$ and $\varrho^\ominus = 997 \text{ kg/m}^3$).

	$k_H^{cp} = \ldots \dfrac{\text{mol}}{\text{m}^3\,\text{Pa}}$	$k_H^{cp} = \ldots \dfrac{\text{M}}{\text{atm}}$	$k_H^{cc} = \ldots$	$k_H^{bp} = \ldots \dfrac{\text{mol}}{\text{kg}\,\text{Pa}}$
$k_H^{cp} = 1 \dfrac{\text{mol}}{\text{m}^3\,\text{Pa}}$	1	101.3	2479	1.003×10^{-3}
$k_H^{cp} = 1 \dfrac{\text{M}}{\text{atm}}$	9.869×10^{-3}	1	24.46	9.899×10^{-6}
$k_H^{cc} = 1$	4.034×10^{-4}	0.04088	1	4.046×10^{-7}
$k_H^{bp} = 1 \dfrac{\text{mol}}{\text{kg}\,\text{Pa}}$	997	1.010×10^{5}	2.471×10^{6}	1

TABLE III

Conversion factors between several inverse Henry's law coefficients $k_{H,\text{inv}}$ representing volatility (at $T^\ominus$ and $\varrho^\ominus = 997 \text{ kg/m}^3$).

	$k_{H,\text{inv}}^{px} = \ldots \text{atm}$	$k_{H,\text{inv}}^{pc} = \ldots \dfrac{\text{m}^3\,\text{Pa}}{\text{mol}}$	$k_{H,\text{inv}}^{cc} = \ldots$
$k_{H,\text{inv}}^{px} = 1 \text{ atm}$	1	1.831	7.386×10^{-4}
$k_{H,\text{inv}}^{pc} = 1 \dfrac{\text{m}^3\,\text{Pa}}{\text{mol}}$	0.5462	1	4.034×10^{-4}
$k_{H,\text{inv}}^{cc} = 1$	1354	2479	1

TABLE IV

Products of Henry's law coefficients k_H representing solubility and inverse Henry's law coefficients $k_{H,\text{inv}}$ representing volatility (at $T^\ominus$ and $\varrho^\ominus = 997 \text{ kg/m}^3$).

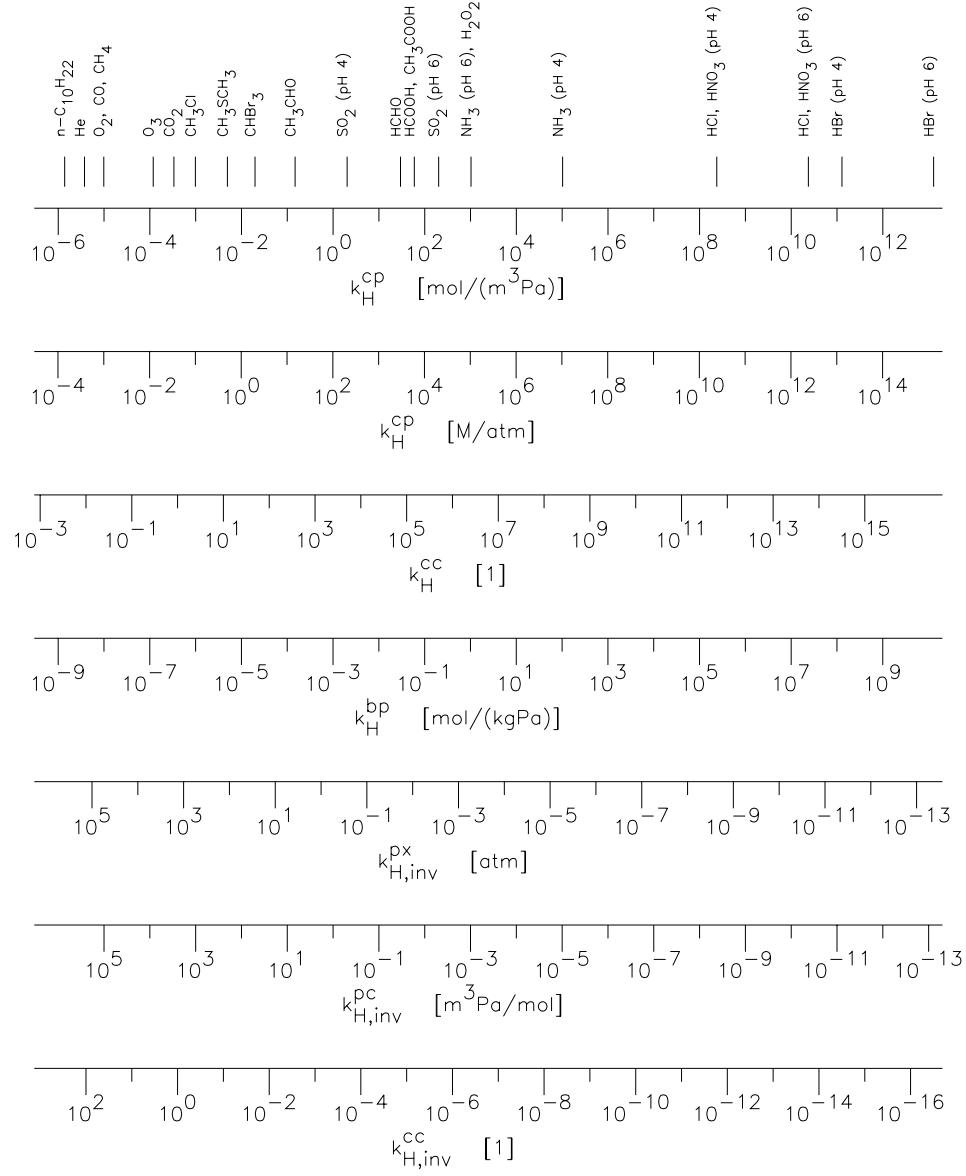|	$\dfrac{k_H^{cp}}{\text{mol}/(\text{m}^3\,\text{Pa})}$	$\dfrac{k_H^{cp}}{\text{M}/\text{atm}}$	$\dfrac{k_H^{cc}}{1}$	$\dfrac{k_H^{bp}}{\text{mol}/(\text{kg}\,\text{Pa})}$
$\dfrac{k_{H,\text{inv}}^{px}}{\text{atm}}$	0.5462	55.34	1354	5.478×10^{-4}
$\dfrac{k_{H,\text{inv}}^{pc}}{\text{m}^3\,\text{Pa}/\text{mol}}$	1	101.3	2479	1.003×10^{-3}
$\dfrac{k_{H,\text{inv}}^{cc}}{1}$	4.034×10^{-4}	0.04088	1	4.046×10^{-7}

Figure 1. Overview of the range of k_H values of some selected species. Note that the effective solubility of acids and bases depends on the solution pH.

2.1.3. *Henry's Law Coefficient Defined via Molality (k_H^{bp})*

There are some advantages to describing the aqueous phase in terms of molality instead of concentration:

$$k_H^{bp} \stackrel{\text{def}}{=} \lim_{b,p \to 0} b/p. \tag{3}$$

Here, b is used as the symbol for molality (instead of m) to avoid confusion with the symbol m for mass. The SI unit for k_H^{bp} is mol/(kg Pa). There is no simple way to calculate k_H^{cp} from k_H^{bp} since the conversion between concentration c_a and molality b involves *all* solutes of a solution. For a solution with a total of n solutes with indices $i = 1, \ldots, n$, the conversion is:

$$c_a = \frac{b\varrho}{1 + \sum_{i=1}^{n} b_i M_i} \tag{4}$$

where ϱ = density of the solution, and M = molar mass. Here, b is identical to one of the b_i in the denominator. If there is only one solute, Equation (4) simplifies to:

$$c_a = \frac{b\varrho}{1 + bM}. \tag{5}$$

Henry's law is only valid for dilute solutions where $bM \ll 1$ and $\varrho \approx \varrho_{H_2O}$. In this case the conversion reduces further to:

$$c_a \approx b\varrho_{H_2O} \tag{6}$$

and thus:

$$k_H^{bp} \approx k_H^{cp}/\varrho_{H_2O}. \tag{7}$$

The molality of a solution does not change with T since it refers to the *mass* of the solvent. In contrast, the concentration c does change with T, since the density of a solution is temperature-dependent. Defining the Henry's law coefficient via b has the advantage that any temperature dependence of k_H^{bp} is a true solubility phenomenon and not introduced indirectly via a density change of the solution. Using a molality-based Henry's law coefficient is also useful for defining Sechenov coefficients (see Section 2.4).

2.1.4. *The Inverse Henry's Law Coefficient Defined via Concentration ($k_{H,inv}^{pc}$)*

A common way to define an inverse Henry's law coefficient is dividing the partial pressure by the aqueous-phase concentration:

$$k_{H,inv}^{pc} \stackrel{\text{def}}{=} \lim_{p,c \to 0} p/c_a = 1/k_H^{cp}. \tag{8}$$

The SI unit for $k_{H,inv}^{pc}$ is Pa m^3/mol.

2.1.5. *The Inverse Henry's Law Coefficient Defined via Aqueous-Phase Mixing Ratio ($k_{H,inv}^{px}$)*

Another inverse Henry's law coefficient is:

$$k_{H,inv}^{px} \overset{\text{def}}{=} \lim_{p,x \to 0} p/x. \tag{9}$$

Here, x is the molar mixing ratio in the aqueous phase. For a dilute, aqueous solution the conversion between x and c_a is:

$$c_a \approx x \frac{\varrho_{H_2O}}{M_{H_2O}}, \tag{10}$$

where ϱ_{H_2O} = density of water and M_{H_2O} = molar mass of water. Thus:

$$k_{H,inv}^{px} \approx \frac{\varrho_{H_2O}}{M_{H_2O} \times k_H^{cp}}. \tag{11}$$

The SI unit for $k_{H,inv}^{px}$ is Pa. However, atm is still frequently used (1 atm = 101325 Pa).

2.1.6. *The Inverse Dimensionless Henry's Law Coefficient $k_{H,inv}^{cc}$*

The inverse Henry's law coefficient can also be expressed as the dimensionless ratio between the gas-phase concentration c_g of a species and its aqueous-phase concentration c_a:

$$k_{H,inv}^{cc} \overset{\text{def}}{=} \lim_{c,c \to 0} c_g/c_a = 1/k_H^{cc}. \tag{12}$$

2.2. Effective Henry's law coefficients k_H^{eff} for acids, bases, and other species with aqueous-phase equilibria

Henry's law applies to the physical solubility of gases. However, in some cases the effective solubility is enhanced by chemical equilibria in the aqueous phase. For example, methanal (HCHO, formaldehyde) is almost completely hydrated in aqueous solution (Betterton, 1992):

$$HCHO + H_2O \rightleftharpoons H_2C(OH)_2. \tag{13}$$

Taking the solubility enhancement due to this equilibrium into account, an effective Henry's law coefficient k_H^{eff} can be defined:

$$k_H^{eff} = k_H \times \frac{[HCHO] + [H_2C(OH)_2]}{[HCHO]}. \tag{14}$$

For HCHO and other aldehydes, tabulated data might implicitly refer to the effective Henry's law coefficient.
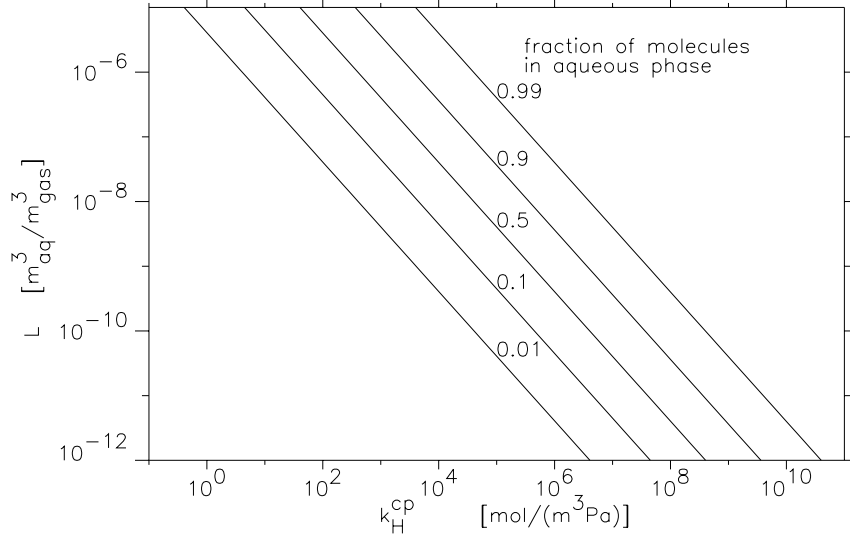
Figure 2. Distribution of atmospheric species between the gas phase and the aqueous phase as a function of its Henry's law coefficient k_H^{cp} and the liquid water content L. The fraction of molecules in the aqueous phase is calculated at $T = T^{\ominus}$ using $N_a/(N_g + N_a) = k_H^{cp} R T L/(1 + k_H^{cp} R T L)$

For acids HA and bases BOH the effective Henry's law coefficients depend on solution pH:

$$k_H^{\text{eff}}(\text{HA}) = k_H(\text{HA}) \left(1 + \frac{K_A}{[\text{H}^+]}\right) \tag{15}$$

$$k_H^{\text{eff}}(\text{BOH}) = k_H(\text{BOH}) \left(1 + \frac{K_B}{[\text{OH}^-]}\right) \tag{16}$$

where $K_A = [\text{H}^+][\text{A}^-]/[\text{HA}]$ = acid constant, and $K_B = [\text{B}^+][\text{OH}^-]/[\text{BOH}]$ = base constant. For strong acids $K_A/[\text{H}^+] \gg 1$, and Equation (15) can be simplified further:

$$k_H^{\text{eff}} \approx \frac{k_H K_A}{[\text{H}^+]}. \tag{17}$$

Instead of including [H$^+$] into the Henry's law coefficient, some authors (e.g., Brimblecombe and Clegg, 1988) present the product $k_H K_A$ and also call it the Henry's law coefficient. One has to be aware, however, that k_H^{eff} and the product $k_H K_A$ are different quantities and have different units!

2.3. HENRY'S LAW FOR NON-IDEAL SOLUTIONS

The definitions of Henry's law coefficients as given in Section 2.1 involve extrapolation to infinite dilution, i.e. to an ideal solution. In order to apply Henry's law to real solutions, activity coefficients γ are introduced. They are dimensionless correction factors that account for the non-ideality of real solutions. The activity coefficients can be defined on the basis of molar mixing ratio (x), concentration (c), or molality (b) which is denoted as a subscript (γ_x, γ_c, γ_b). At infinite dilution, γ approaches unity:

$$\lim_{x \to 0} \gamma_x = \lim_{c \to 0} \gamma_c = \lim_{b \to 0} \gamma_b = 1. \tag{18}$$

The non-ideality of the gas phase is described in a similar way. The fugacity coefficient φ is the correction factor for the pressure p. At vanishing pressure, φ approaches unity:

$$\lim_{p \to 0} \varphi = 1 \tag{19}$$

Although it would also be possible to express the non-ideality of the gas phase on the basis of concentration, fugacity coefficients (based on pressure) are used exclusively.

Now the Henry's law coefficients can be defined under non-ideal conditions without the need to extrapolate to infinite dilution. It is only necessary to make the following substitutions:

$$x \ \to \ \gamma_x x, \tag{20}$$
$$c \ \to \ \gamma_c c, \tag{21}$$
$$b \ \to \ \gamma_b b, \tag{22}$$
$$p \ \to \ \varphi p. \tag{23}$$

This yields:

$$k_{\mathrm{H}}^{cp} \ = \ \frac{\gamma_c c_{\mathrm{a}}}{\varphi p}, \tag{24}$$

$$k_{\mathrm{H}}^{bp} \ = \ \frac{\gamma_b b}{\varphi p}, \tag{25}$$

$$k_{\mathrm{H,inv}}^{pc} \ = \ \frac{\varphi p}{\gamma_c c_{\mathrm{a}}}, \tag{26}$$

$$k_{\mathrm{H,inv}}^{px} \ = \ \frac{\varphi p}{\gamma_x x}. \tag{27}$$

Since there is no gas-phase correction factor on the basis of concentration, the Henry's law coefficients k_{H}^{cc} and $k_{\mathrm{H,inv}}^{cc}$ are only used for ideal systems. Experimental ways to determine fugacity and activity coefficients can be found in textbooks of physical chemistry (e.g., Atkins, 1986).

2.4. THE SALTING OUT EFFECT

The solubility of a gas in pure water is larger than that in a salt solution. This so-called salting out effect can be approximated with the Sechenov (Setchenow, Setschenow) equation (Pitzer, 1991):

$$\log \left(\frac{k_H^0}{k_H} \right) = k_s^c \times c(\text{salt}), \tag{28}$$

where k_H = Henry's law coefficient in salt solution, k_H^0 = Henry's law coefficient in pure water, k_s^c = concentration-based Sechenov coefficient, and $c(\text{salt})$ = concentration of salt.

There are many alternative ways to define the Sechenov equation, depending on how k_H and the aqueous-phase composition are described (on the basis of concentration, molality, molar fraction, ...). It is probably best to define the salt solution on the basis of molality:

$$\log \left(\frac{k_H^0}{k_H} \right) = k_s^b \times b(\text{salt}). \tag{29}$$

Adding dry salt to a solution does not change the molality of other solutes since the molality refers to the mass of the *solvent*, not the mass of the *solution*. In contrast, adding salt to a solution increases its volume and thus decreases the concentrations of its other solutes. A non-zero Sechenov coefficient would be obtained from Equation (28) even without degassing of the solution. For the same reason, the molar fraction x is equally unsuitable to define the Sechenov coefficient.

Battino et al. (1995) list 30 different definitions and show some conversions between them. Conversion between concentration- and molality-based Sechenov coefficients is quite complex. Equation (4) must be used which requires knowledge of all solutes as well as of the density of the solution. Published data often does not provide this information.

Introducing the Sechenov coefficient can improve modeling of concentrated solutions like sulfate or sea-salt aerosol particles. Unfortunately, literature data is rare and the salting out effect has been described quantitatively only for a few gases yet (e.g., De Bruyn et al., 1995).

2.5. TEMPERATURE DEPENDENCE OF HENRY'S LAW COEFFICIENTS

The temperature dependence of equilibrium constants can generally be described with the van't Hoff equation (e.g., Atkins, 1986). It also applies to Henry's law coefficients:

$$\frac{d \ln k_H}{d(1/T)} = \frac{-\Delta_{\text{soln}} H}{R}, \tag{30}$$

where $\Delta_{\mathrm{soln}}H$ = enthalpy of dissolution. Integrating and choosing $k_{\mathrm{H}}^{\ominus}$ at $T^{\ominus} = 298.15$ K as reference leads to:

$$k_{\mathrm{H}}(T) = k_{\mathrm{H}}^{\ominus} \times \exp\left(\frac{-\Delta_{\mathrm{soln}}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right) \tag{31}$$

Henry's law data is often tabulated as $k_{\mathrm{H}}^{\ominus}$ and $\Delta_{\mathrm{soln}}H/R$. Alternatively, one can use the expression

$$k_{\mathrm{H}}(T) = A \times \exp\frac{B}{T} \tag{32}$$

and tabulate the parameters A and B. Here, $k_{\mathrm{H}}^{\ominus} = A \times \exp(B/T^{\ominus})$ and $\Delta_{\mathrm{soln}}H/R = -B$. Since $k_{\mathrm{H}}^{\ominus}$ depends exponentially on B, it is important that B is reported with sufficient significant digits.

The van't Hoff equation is only valid for a limited temperature range. Some authors use different, empirical ways to describe the temperature dependence in order to cover a larger temperature range. Sometimes (e.g., Wilhelm et al., 1977) the temperature dependence is expressed as a function of the parameters A, B, C, and D:

$$\ln k_{\mathrm{H}} = A + B \times \left(\frac{T}{\mathrm{K}}\right)^{-1} + C \times \ln\left(\frac{T}{\mathrm{K}}\right) + D \times \left(\frac{T}{\mathrm{K}}\right). \tag{33}$$

Note that the temperature dependences for k_{H}^{cp} and k_{H}^{cc} are different since the conversion factor between them includes the temperature:

$$
\begin{aligned}
k_{\mathrm{H}}^{cp} &= k_{\mathrm{H}}^{cc}/(RT) \\
\Leftrightarrow \ln k_{\mathrm{H}}^{cp} &= \ln k_{\mathrm{H}}^{cc} + \ln(1/R) + \ln(1/T) \\
\Rightarrow \frac{\mathrm{d}\ln k_{\mathrm{H}}^{cp}}{\mathrm{d}(1/T)} &= \frac{\mathrm{d}\ln k_{\mathrm{H}}^{cc}}{\mathrm{d}(1/T)} + \frac{\mathrm{d}\ln(1/T)}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln k_{\mathrm{H}}^{cc}}{\mathrm{d}(1/T)} + T
\end{aligned}
\tag{34}
$$

2.6. Obtaining Henry's law coefficients

Henry's law coefficients are needed for atmospheric modeling. However, it is often difficult to find them in the literature. Several ways to get k_{H} values directly or indirectly are shown below.

2.6.1. *Data Tables*
Many Henry's law coefficients have been published in data tables. A large such compilation of more than 500 Henry's law coefficients is available on the internet (Sander, 1996). Other useful references are Mackay and Shiu (1981), Betterton (1992), and Staudinger and Roberts (1996).

2.6.2. *Quantitative Property Property Relationships*

If the Henry's law coefficient is not available for a specific species, it might be possible to derive it from other physical properties of that species. This method is called quantitative property property relationship (QPPR). It has recently been reviewed by Staudinger and Roberts (1996) and only a short summary is given here. If the solubility of a liquid or solid is low, a saturated solution still qualifies as a dilute solution. In this case the Henry's law coefficient is:

$$k_H^{cp} = \frac{c_{a,sat}}{p^*} \tag{35}$$

with $c_{a,sat}$ = concentration of a saturated solution and p^* = vapor pressure of the solute in pure form. Concentrations of saturated solutions are listed in Stephen and Stephen (1963). Vapor pressure data can be found in Lide and Frederikse (1995).

It is also possible to multiply the infinite dilution activity coefficient γ^∞ with p^*:

$$k_{H,inv}^{px} = p^* \times \gamma^\infty \tag{36}$$

A database of γ^∞ values has been published by Kojima et al. (1997). Note that γ^∞ is referenced to Raoult's law and not to Henry's law. It thus does not approach unity at infinite dilution (Mackay et al., 1979). See also Nielsen et al. (1994) for more information about the relation between infinite dilution activity coefficients and k_H.
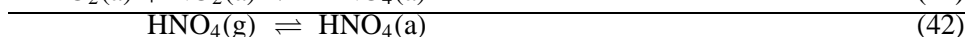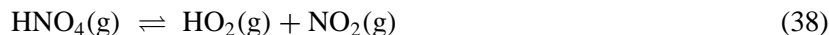
2.6.3. *Thermodynamic Calculations*

Another way to obtain Henry's law coefficients is to use the relationship between the free enthalpy and the corresponding equilibrium constant. Applied to Henry's law, the equation is:

$$k_H = \exp\left(\frac{\Delta_{soln}G}{RT}\right) \tag{37}$$

The free enthalpy of dissolution $\Delta_{soln}G$ is the difference between the free enthalpies of formation $\Delta_{f,a}G$ in the aqueous phase and $\Delta_{f,g}G$ in the gas phase, respectively. Strictly speaking, the expression on the right hand side of Equation (37) is just a dimensionless number. The unit and type of k_H are determined by the standard state on which $\Delta_{soln}G$ is based. Free enthalpy values are tabulated in Wagman et al. (1982). Their values refer to the standard states of $p = 10^5$ Pa and $b = 1$ mol/kg. Equation (37) thus yields the molality-based Henry's law coefficient k_H^{bp}. As an example, for HOCl values of $\Delta_{f,a}G$ = -79.9 kJ/mol and $\Delta_{f,g}G$ = -66.1 kJ/mol are listed. From this, a Henry's law coefficient of k_H^{bp} = 262 mol kg^{-1} (10^5 Pa)$^{-1}$ can be calculated at $T^\ominus$.

2.6.4. *Reaction Cycles*

It is also possible to obtain k_H by constructing a cyclic process (similar to a Haber-Born cycle) in which the Henry's law coefficient is the only unknown. For example, Régimbal and Mozurkewich (1997) considered the following cycle:

$$HNO_4(g) \rightleftharpoons HO_2(g) + NO_2(g) \tag{38}$$

$$HO_2(g) \rightleftharpoons HO_2(a) \tag{39}$$

$$NO_2(g) \rightleftharpoons NO_2(a) \tag{40}$$

$$HO_2(a) + NO_2(a) \rightleftharpoons HNO_4(a) \tag{41}$$

$$\overline{HNO_4(g) \rightleftharpoons HNO_4(a)} \tag{42}$$

Using available data for equilibria (38)–(41) they were able to calculate the Henry's law coefficient for HNO_4.

2.6.5. *Quantitative Structure Property Relationships*

Henry's law coefficients can be approximated by extrapolating data from structurally related compounds. This so-called 'Quantitative structure property relationship' (QSPR) method has been reviewed by Staudinger and Roberts (1996). In a very simplified form, this approach has been used by Jacob (1986) to estimate $k_H(CH_3OO)$ based on three known values:

$$k_H(CH_3OO) \approx k_H(HOO) \times \frac{k_H(CH_3OOH)}{k_H(HOOH)}. \tag{43}$$

In more complex studies up to a few hundred k_H values were used as a base set to develop QSPRs. QSPRs are usually less reliable than other methods but they provide a good estimate if no other data are available.

This method must be used with care. Frenzel et al. (1998) estimated that $k_H(BrCl)$ is the average of $k_H(Br_2)$ and $k_H(Cl_2)$. However, experimental data by Dubik et al. (1987) shows that BrCl is more soluble that either Br_2 or Cl_2. This could be due to the fact that BrCl has a non-zero dipole moment.

3. Non-Equilibrium Kinetics: Mass Transfer of Chemicals between the Phases

Henry's law is only valid for equilibrium conditions. In some cases the equilibrium is never reached, for example if an aqueous-phase reaction consumes a compound faster than it can be replaced from the gas phase (e.g., the oxidation of aqueous S(IV) by ozone at high pH). The equilibration process, as shown in Figure 3, consists of the following steps: 1) Gas-phase diffusion to (and from) the surface of the droplet, 2) Interfacial mass transport through the gas-liquid phase boundary, and 3) Aqueous-phase diffusion and chemical reactions in the droplet.

These processes will be treated separately in the next sections. The system quickly reaches a steady state with stationary concentration profiles in both phases.
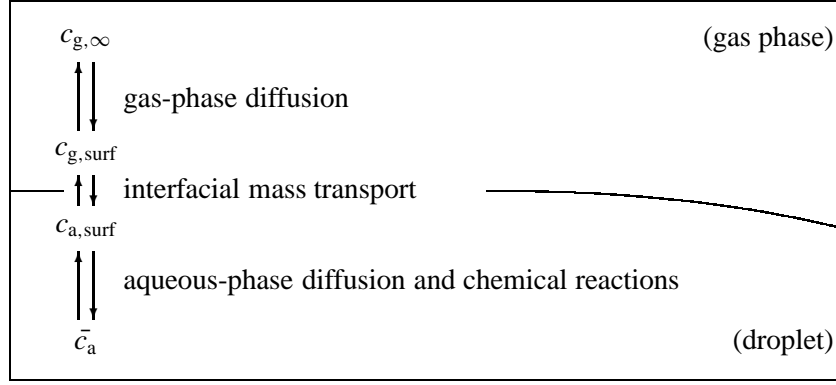
Figure 3. Processes involved in the equilibration of the gas phase and a droplet.

A justification for the steady state assumption can be found in Schwartz (1986). Prominent points of this profile are:

— $c_{g,\infty}$ = background gas-phase concentration far away from the droplet
— $c_{g,surf}$ = gas-phase concentration at surface (outside of the droplet)
— $c_{a,surf}$ = aqueous-phase concentration at surface (inside the droplet)
— $\bar{c}_a$ = average aqueous-phase concentration

In the following two sections rate coefficients for gas-phase diffusion and the interfacial mass transport will be derived. Readers who are only interested in the results may continue with Section 3.3 where it is shown how the combined effects of gas-phase diffusion and interfacial mass transport can be described using a single first order rate coefficient.

3.1. GAS-PHASE DIFFUSION TO A SPHERICAL DROPLET (CONTINUUM REGIME)

Transport by diffusion is sometimes called the 'continuum' regime and thus identified by the subscript c. The gas-phase diffusion flux J_c is described using Fick's first law:

$$J_c = \frac{1}{A}\frac{dn}{dt} = -D_g\frac{dc}{dx} \tag{44}$$

where A = area [m^2], n = amount of substance [mol], t = time [s], D_g = gas-phase diffusivity [m^2/s], and x = path along which diffusion takes place [m].

In the case of diffusion towards a spherical droplet, x is in the direction of the radius and the area is $A = 4\pi x^2$. The flux J_c increases with decreasing distance to the particle. However, the flow $\tilde{J}_c = dn/dt$ will be independent of x once a stationary concentration profile has been reached:

$$\tilde{J}_c = J_c A = \frac{dn}{dt} = -D_g(4\pi x^2)\frac{dc}{dx} \tag{45}$$

$$\frac{d\tilde{J}_c}{dx} = -4\pi D_g d\left(x^2 \frac{dc}{dx}\right)/dx = 2x \frac{dc}{dx} + x^2 \frac{d^2c}{dx^2} = 0. \tag{46}$$

This differential equation has the solutions:

$$c(x) = C_1 + C_2/x \tag{47}$$

The integration constants C_1 and C_2 can be determined with the boundary conditions. At a large distance from the droplet, the concentration is the background gas-phase concentration $c_{g,\infty}$:

$$\lim_{x\to\infty} c(x) = c_{g,\infty} \Rightarrow C_1 = c_{g,\infty}. \tag{48}$$

Now, consider a droplet with radius r. At $x = r$, thus at the surface of the droplet, the gas-phase concentration is $c_{g,surf}$:

$$c(r) = c_{g,surf} = C_1 + C_2/r \Rightarrow C_2 = (c_{g,surf} - c_{g,\infty})r \tag{49}$$

C_1 and C_2 are inserted into Equation (47). The concentration profile is:

$$c(x) = c_{g,\infty} + \frac{(c_{g,surf} - c_{g,\infty})r}{x}. \tag{50}$$

Under atmospheric conditions, the distance between two aerosol particles is much larger than their radiii. For an average location in the gas phase, the distance x to the nearest droplet is $x \gg r$ and thus $c(x) \approx c_{g,\infty}$. Only near the droplet surface, the deviation from the background concentration must be considered. The gradient of the concentration profile is:

$$\frac{dc}{dx} = \frac{(c_{g,\infty} - c_{g,surf})r}{x^2}. \tag{51}$$

At the droplet surface ($x = r$), the gradient is:

$$\left(\frac{dc}{dx}\right)_{x=r} = \frac{c_{g,\infty} - c_{g,surf}}{r}. \tag{52}$$

This can be inserted into Equation (44) to obtain the flux near the surface:

$$J_c = \frac{1}{A}\frac{dn}{dt} = -D_g \frac{c_{g,\infty} - c_{g,surf}}{r}. \tag{53}$$

With $V = 4/3\,\pi r^3$ being the droplet volume and $A = 4\pi r^2$ being the droplet surface, the concentration change in the aqueous-phase is:

$$\begin{aligned}
\frac{dc_a}{dt} &= -\frac{\tilde{J}_c}{V} = -\frac{A}{V}J_c \\
&= \frac{4\pi r^2}{4/3\,\pi r^3} D_g \frac{c_{g,\infty} - c_{g,surf}}{r} \\
&= \frac{3D_g}{r^2}(c_{g,\infty} - c_{g,surf}).
\end{aligned} \tag{54}$$

Thus a first-order rate coefficient for the gas-phase diffusion process can be defined as:

$$k_{dg} = \frac{3D_g}{r^2}. \tag{55}$$

Introducing the mean free path λ [m] and substituting $3D_g = \lambda\bar{v}$ (e.g., Atkins, 1986) results in:

$$k_{dg} = \frac{\lambda\bar{v}}{r^2}. \tag{56}$$

3.2. INTERFACIAL MASS TRANSPORT AND THE ACCOMMODATION COEFFICIENT (KINETIC REGIME)

Interfacial mass transport as treated in this section is sometimes called the 'free molecular' or the 'kinetic' regime. It is identified by the subscript k here. Not all the molecules reaching the surface of the droplet will be incorporated into the aqueous-phase. The probability of a phase transition into the droplet is indicated by the accommodation coefficient α. To obtain J_k^{in}, the flux through phase boundary into the droplet, the accommodation coefficient has to be multiplied with the flux J_x [mol m^{-2} s^{-1}] towards the surface:

$$J_k^{in} = \frac{1}{A}\frac{dn}{dt} = \alpha J_x. \tag{57}$$

The flux J_x is the product of the mean molecular velocity along the x-axis $\bar{v}_x$ [m/s] and the gas-phase concentration at the droplet surface $c_{g,surf}$:

$$J_x = c_{g,surf}\bar{v}_x. \tag{58}$$

According to the Maxwell-Boltzmann distribution of velocity, $\bar{v}_x$ is:

$$\bar{v}_x = -\frac{1}{4}\bar{v} = -\frac{1}{4}\sqrt{\frac{8RT}{M\pi}} \tag{59}$$

where $\bar{v}$ = mean molecular velocity [m/s] and M = molar mass [kg/mol]. The negative value of $\bar{v}_x$ indicates motion towards $x = 0$, the center of the droplet. The above equations can be combined:

$$J_k^{in} = -\frac{\bar{v}\alpha}{4}c_{g,surf}. \tag{60}$$

The flux in the opposite direction must also be considered. The driving force behind the flux out of the droplet is the aqueous-phase concentration $c_{a,surf}$ near the surface of the droplet. In analogy to Equation (60) the flux is described as:

$$J_k^{out} = \frac{\bar{v}_a\alpha_a}{4}c_{a,surf} \tag{61}$$

where $\bar{v}_a$ is the aqueous-phase mean molecular velocity and α_a is the aqueous-phase accommodation coefficient describing the probability that an aqueous-phase molecule reaching the surface will cross the interface and leave the droplet. The net flux J_k is:

$$J_k = J_k^{\text{out}} + J_k^{\text{in}} = \frac{\bar{v}_a \alpha_a}{4} c_{a,\text{surf}} - \frac{\bar{v}\alpha}{4} c_{g,\text{surf}}. \tag{62}$$

Under equilibrium conditions, $J_k = 0$ and $c_{a,\text{surf}}^{\text{eq}}/c_{g,\text{surf}}^{\text{eq}} = k_H^{cc}$. Thus:

$$\frac{\bar{v}_a \alpha_a}{4} c_{a,\text{surf}}^{\text{eq}} = \frac{\bar{v}\alpha}{4} c_{g,\text{surf}}^{\text{eq}} \Leftrightarrow \frac{c_{a,\text{surf}}^{\text{eq}}}{c_{g,\text{surf}}^{\text{eq}}} = \frac{\bar{v}\alpha}{\bar{v}_a \alpha_a} = k_H^{cc} \tag{63}$$

k_H^{cc} is inserted into Equation (62):

$$J_k = \frac{\bar{v}\alpha}{4} \left(\frac{c_{a,\text{surf}}}{k_H^{cc}} - c_{g,\text{surf}} \right). \tag{64}$$

The notion of an aqueous-phase accommodation coefficient α_a has not been introduced previously but it serves as a convenient way to derive Equation (64). Usually, the appearence of k_H^{cc} in the equation is explained as a 'scaling factor' to convert between c_g and c_a. The concentration change in the aqueous-phase is:

$$\begin{aligned}
\frac{dc_a}{dt} &= -\frac{A}{V} J_k \\
&= -\frac{4\pi r^2}{4/3\,\pi r^3} \frac{\bar{v}\alpha}{4} \left(\frac{c_{a,\text{surf}}}{k_H^{cc}} - c_{g,\text{surf}} \right) \\
&= \frac{3\bar{v}\alpha}{4r} \left(c_{g,\text{surf}} - \frac{c_{a,\text{surf}}}{k_H^{cc}} \right).
\end{aligned} \tag{65}$$

Thus a first-order rate coefficient for the interfacial mass transport process can be defined as:

$$k_i = \frac{3\bar{v}\alpha}{4r}. \tag{66}$$

A small accommodation coefficient α does not necessarily represent a low solubility but only a slow equilibration.

3.3. THE MASS TRANSFER COEFFICIENT k_{mt}

So far gas-phase diffusion and interfacial mass transport were considered separately. The flux of molecules to the droplet surface is given by Equation (53) and the flux through the phase boundary is given by Equation (64). Since a stationary profile is assumed, these fluxes must be identical (otherwise the surface concentration $c_{g,\text{surf}}$ would change):

$$J_c = J_k \Leftrightarrow -\frac{D_g}{r}(c_{g,\infty} - c_{g,\text{surf}}) = \frac{\bar{v}\alpha}{4} \left(\frac{c_{a,\text{surf}}}{k_H^{cc}} - c_{g,\text{surf}} \right). \tag{67}$$
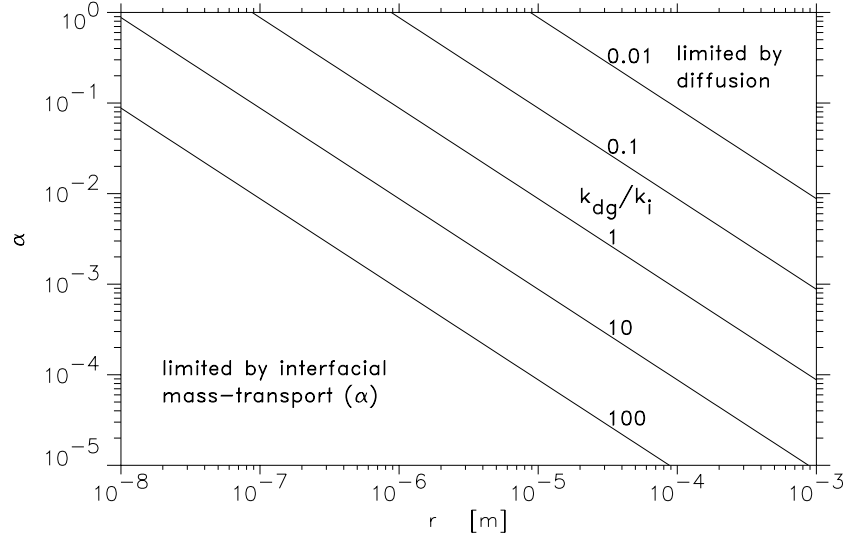
Figure 4. The ratio k_{dg}/k_i as a function of droplet radius r and accommodation coefficient α (calculated using equations (66) and (56) at a free path of $\lambda = 66$ nm)

This can be rearranged to get an expression for $c_{g,surf}$. Inserting $c_{g,surf}$ into either Equation (54) or Equation (65) yields in a lengthy but straightforward transformation:

$$\frac{dc_a}{dt} = k_{mt} \left(c_{g,\infty} - \frac{c_{a,surf}}{k_H^{cc}} \right). \tag{68}$$

Here, k_{mt} is called the mass transfer coefficient and its definition is:

$$k_{mt} = \left(\frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha} \right)^{-1}. \tag{69}$$

This value of k_{mt} was introduced by Schwartz (1986). It is used in many modeling studies (e.g., Lelieveld and Crutzen, 1991, Chameides and Stelson, 1992, Sander and Crutzen, 1996). Written differently, the relation of k_{mt} to k_{dg} and k_i can be seen:

$$k_{mt} = \left(\frac{1}{k_{dg}} + \frac{1}{k_i} \right)^{-1}. \tag{70}$$

Usually, the unit of k_{mt} is simply said to be s^{-1}. It is important to remember, though, that k_{mt} contains the conversion from m$_{air}^{-3}$ to m$_{aq}^{-3}$. At large radii, k_{mt} is mainly determined by D_g. At small radii, k_{mt} is mainly determined by α (see Figure 4).

In the above derivation of k_{mt} it was assumed that at the droplet surface the transport suddenly switches from the continuum regime (J_c) to the kinetic regime (J_k). However, this is just an approximation. Several ways have been proposed for
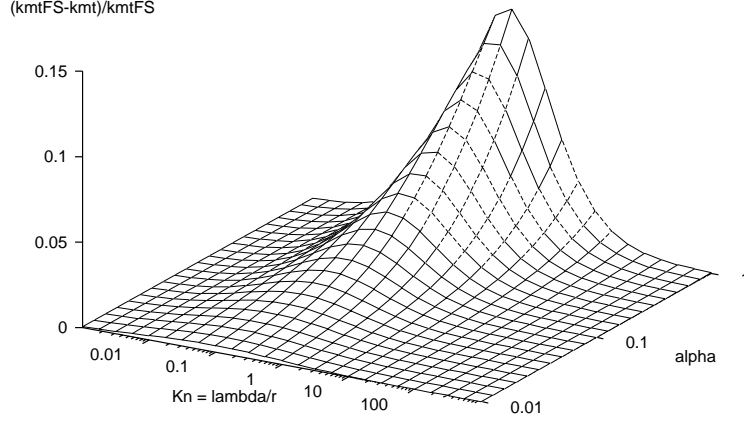
Figure 5. The relative difference between the transfer coefficients k_{mt} and k_{mt}^{FS}

a steady transition from J_c to J_k in the vicinity of the droplet surface. This so-called flux-matching problem was recently reviewed by Seinfeld and Pandis (1998). One solution was given by Fuchs and Sutugin (1971). It is frequently used in models of atmospheric chemistry (e.g., Bower et al., 1991, Chameides and Davis, 1982, Pandis and Seinfeld, 1989). They obtained a slightly different formula for the transfer coefficient, called k_{mt}^{FS} here:

$$k_{mt}^{FS} = \frac{\lambda \bar{v}}{\left(1 + \left(\lambda_{Sa} + 4\frac{1-\alpha}{3\alpha}\right)\frac{\lambda}{r}\right) r^2}. \tag{71}$$

They use the so-called 'linear extrapolation distance' λ_{Sa}, a dimensionless number adopted from Sahni (1966) which can be interpolated as:

$$\lambda_{Sa} \approx \frac{4/3 + 0.71 r/\lambda}{1 + r/\lambda}. \tag{72}$$

At first sight, equations (69) and (71) look quite different. Since both transfer coefficients are frequently used in atmospheric modeling, a comparison between them is shown here. First, Equation (71) is rearranged and the expression for λ_{Sa} is inserted:

$$k_{mt}^{FS} = \left(\frac{r^2}{\lambda \bar{v}}\left(1 - \frac{0.62}{1 + r/\lambda}\right) + \frac{4r}{3\bar{v}\alpha}\right)^{-1}. \tag{73}$$

The relative difference between the transfer coefficients k_{mt} and $k_{\mathrm{mt}}^{\mathrm{FS}}$ is:

$$\frac{k_{\mathrm{mt}}^{\mathrm{FS}} - k_{\mathrm{mt}}}{k_{\mathrm{mt}}^{\mathrm{FS}}} = \frac{0.62}{(1 + r/\lambda)(1 + \frac{4\lambda}{3\alpha r})}. \tag{74}$$

It depends on α and on the ratio of the free path to the droplet radius. The latter is also called the Knudsen number Kn:

$$\mathrm{Kn} = \lambda/r. \tag{75}$$

Since the right hand term of Equation (74) is positive, k_{mt} is always smaller than $k_{\mathrm{mt}}^{\mathrm{FS}}$. From the plot in Figure 5 it can be seen that the relative difference is only significant around Kn ≈ 1 and is always below 15 %. For many species of atmospheric relevance this difference is much smaller than the uncertainties associated with k_{H} and α. Both formulae will give undistinguishable results within the error limits. k_{mt} has the advantage over $k_{\mathrm{mt}}^{\mathrm{FS}}$ that it could be derived from relatively few assumptions without the need to define the parameter λ_{Sa}. Using the simple definition of k_{mt} in Equation (69) instead of $k_{\mathrm{mt}}^{\mathrm{FS}}$ in (71) might also save some computing time in complex models.

3.4. AQUEOUS-PHASE DIFFUSION AND CHEMICAL REACTIONS

Once the molecules have crossed the phase border, aqueous-phase diffusion will distribute them throughout the droplet. In the absence of chemical reactions, the concentration c_{a} will eventually be identical to the surface concentration $c_{\mathrm{a,surf}}$ everywhere. However, if fast aqueous-phase reactions destroy the molecules, diffusion will no longer be able to maintain the flat concentration profile. Instead, c_{a} will decrease towards the center of the droplet and the average concentration $\bar{c}_{\mathrm{a}}$ will be less than $c_{\mathrm{a,surf}}$. For a first-order reaction with constant k_{a}, the chemical loss rate is:

$$\frac{\mathrm{d}c_{\mathrm{a}}}{\mathrm{d}t} = k_{\mathrm{a}}\bar{c}_{\mathrm{a}}. \tag{76}$$

Schwartz and Freiberg (1981) have developed a formula for this case to describe the ratio $Q = \bar{c}_{\mathrm{a}}/c_{\mathrm{a,surf}}$:

$$Q = \frac{\bar{c}_{\mathrm{a}}}{c_{\mathrm{a,surf}}} = 3\left(\frac{\coth q}{q} - \frac{1}{q^2}\right). \tag{77}$$

The dimensionless parameter q is defined as:

$$q = r\sqrt{\frac{k_{\mathrm{a}}}{D_{\mathrm{a}}}} \tag{78}$$

where D_{a} is the aqueous-phase diffusion coefficient [m^2/s]. Using this expression, an effective first-order rate constant can be defined as $k_{\mathrm{a}}^{\mathrm{eff}} = k_{\mathrm{a}}Q$ yielding:

$$\frac{\mathrm{d}c_{\mathrm{a}}}{\mathrm{d}t} = k_{\mathrm{a}}^{\mathrm{eff}} c_{\mathrm{a,surf}}. \tag{79}$$

It is interesting to check under which conditions the aqueous-phase diffusion will limit the overall rate. On the one hand, $\bar{c}_a/c_{a,surf}$ as defined in Equation (77) will be significantly less than 1 only for $q > 1$, i.e.:

$$q = r\sqrt{\frac{k_a}{D_a}} > 1 \Leftrightarrow k_a > \frac{D_a}{r^2} \tag{80}$$

On the other hand, aqueous-phase diffusion will not be the limiting factor if the aqueous phase reaction is very fast. If k_a is larger than k_{mt}, basically all molecules reaching the droplet will react immediately and the overall rate depends only on the flux into the droplet. Thus, the range where aqueous-phase diffusion is important is given by:

$$\frac{D_a}{r^2} < k_a < k_{mt}. \tag{81}$$

3.5. CHARACTERISTIC TIMES

In order to get an idea about the timescales involved in mass-transport processes, several expressions have been developed. Some definitions differ by a factor of about two or three (see e.g. Schwartz and Freiberg, 1981, Schwartz, 1986, Seinfeld and Pandis, 1998). Essentially, characteristic times are lifetimes defined as the inverse of the corresponding first-order reaction rates:

$$\tau_{dg} = 1/k_{dg} \quad \text{(for gas-phase diffusion)}, \tag{82}$$
$$\tau_i = 1/k_i \quad \text{(for interfacial mass transport)}, \tag{83}$$
$$\tau_{mt} = 1/k_{mt} = \tau_{dg} + \tau_i, \tag{84}$$
$$\tau_a^{eff} = 1/k_a^{eff} \quad \text{(for aqueous-phase diffusion and reactions)}. \tag{85}$$

The rate-limiting step of the overall process will be the one with the largest characteristic time. See Figure 4 for a comparison of k_{dg} and k_i. It is important to note that these lifetimes describe *aqueous-phase* species. To get the lifetimes of the corresponding gas-phase species, it is necessary to calculate the rate of change of the gas-phase concentration. Mass transfer processes do not change the total concentration c_T of an air parcel, which is defined as:

$$c_T = (1 - L)c_g + Lc_a \tag{86}$$

where L = liquid water content [m_{aq}^3/m_{air}^3]. Since $L \ll 1$, the term $(1 - L)$ can be neglected and the conversion between c_g and c_a is:

$$c_g = c_T - Lc_a. \tag{87}$$

Differentiation with respect to time yields:

$$\frac{dc_g}{dt} = -L\frac{dc_a}{dt}. \tag{88}$$

HCl is a good example to illustrate the difference between gas-phase and aqueous-phase lifetimes: For aerosol particles of $r = 1\,\mu$m, the transfer coefficient for HCl is on the order of $k_{\text{mt}} \approx 10^7$ s^{-1}. When a sea-salt aerosol particle is acidified (e.g., due to uptake of gaseous H_2SO_4) it will start losing chloride. Outgassing of HCl only takes about 10^{-7} s until the aqueous-phase equilibrium is reached. On the other hand, when a plume of HCl is advected over the ocean, alkaline sea-salt aerosol particles will start to scavenge HCl from the gas phase. At a sea-salt liquid water content of $L = 10^{-11}$, the lifetime of gas-phase HCl with respect to scavenging will be $k_{\text{mt}}^{-1} \times L^{-1} = 10^4$ s ≈ 1 hour.

3.6. OBTAINING ACCOMMODATION COEFFICIENTS

Some α values can be found in Nathanson et al. (1996) and in the JPL data tables (DeMore et al., 1997). A compilation of accommodation coefficients has been put on the internet by Müller (1998).

Experimental studies often present an observed uptake coefficient γ instead of the accommodation coefficient α. Whereas α as defined in Equation (64) considers the aqueous-phase concentration as well as the gas-phase concentration, γ only considers the latter:

$$\frac{1}{A}\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\bar{v}\alpha}{4}\left(\frac{c_{\text{a,surf}}}{k_{\text{H}}^{cc}} - c_{\text{g,surf}}\right) = -\frac{\bar{v}\gamma}{4}c_{\text{g,surf}}. \tag{89}$$

If the aqueous-phase concentration is zero (and thus $c_{\text{a,surf}}/k_{\text{H}}^{cc} = 0$), then α equals γ. Otherwise, $\gamma < \alpha$. If no α values are available, γ can be used as a lower limit. However, if $\gamma \ll \alpha$, one has to be aware that using γ instead of α could lead to the false conclusion that phase transport is limited by interfacial mass transport.

In some cases an upper limit for α can be obtained by rearranging Equation (63):

$$\alpha = k_{\text{H}}^{cc} \times \frac{\bar{v}_{\text{a}}}{\bar{v}} \times \alpha_{\text{a}}. \tag{90}$$

It is probably safe to assume that the mean molecular velocity in the aqueous phase $\bar{v}_{\text{a}}$ is not larger than that in the gas phase $\bar{v}$. The aqueous-phase accommodation coefficient α_{a} cannot be larger than 1. Thus: $\alpha \leq k_{\text{H}}^{cc}$. Obviously, this relation is only useful for species of very low solubility with $k_{\text{H}}^{cc} < 1$.

4. Representation of Particle Size Distributions in Models

4.1. THE SIZE DISTRIBUTION FUNCTION $\mathrm{d}N(r)/\mathrm{d}r$

In the preceeding section it was shown that the rate of transport between the phases depends on the size of the particles, i.e. the radius r of the droplets. Thus it is necessary to find a way to describe the size distribution in computer modeling. In the simplest case, a monodisperse population is assumed, i.e. all particles have

the same radius r. In that case, application of the equations defining k_{dg}, k_i, and k_a^{eff} is straightforward. However, for a more realistic description of clouds and aerosol particles it is necessary to consider particles of different sizes. Therefore, the function $N(r)$ is defined to be the number concentration of aerosol particles with a radius smaller than r. The SI unit of $N(r)$ is $1/m^3$.

The particle concentration in the size range $r_1 < r < r_2$ is $\Delta N = N(r_2) - N(r_1)$. It is also possible to obtain ΔN by integrating $dN(r)/dr$ from r_1 to r_2:

$$\Delta N = \int_{r_1}^{r_2} \left(\frac{dN(r)}{dr}\right) dr = \int_{r_1}^{r_2} dN(r) = N(r_2) - N(r_1). \tag{91}$$

The total number concentration of aerosol particles N_{tot} is obtained by integrating over the entire size range:

$$N_{tot} = \int_0^\infty \left(\frac{dN(r)}{dr}\right) dr. \tag{92}$$

Though sometimes the symbol N is used for both N_{tot} as well as $N(r)$ it is important to notice the difference: N_{tot} is a single value whereas $N(r)$ is a function of r. Incidently, N_{tot} equals $N(\infty)$.

Often the size distribution $dN(r)/dr$ is introduced without actually defining the function $N(r)$ correctly. Please note that $N(r)$ is *not* 'the number of particles between r and $r + dr$'!

To visualize a size range of several orders of magnitude, often $dN(r)/d(\lg r)$ is plotted vs. $\lg r$ instead of $dN(r)/dr$ vs. r. The relation between these size distributions is:

$$\frac{dN(r)}{d\lg r} = \frac{dN(r)}{dr} \times \frac{r}{\lg e}. \tag{93}$$

The distribution of the aerosol volume V and the surface area A is given by:

$$\frac{dV(r)}{dr} = \frac{4}{3}\pi r^3 \times \frac{dN(r)}{dr}, \tag{94}$$

$$\frac{dA(r)}{dr} = 4\pi r^2 \times \frac{dN(r)}{dr}. \tag{95}$$

Here $V(r)$ is the volume of all particles with a radius smaller than r and $A(r)$ is the surface of all particles with a radius smaller than r. On a logarithmic scale these equations become:

$$\frac{dV(r)}{d\lg r} = \frac{4}{3}\pi r^3 \times \frac{dN(r)}{d\lg r}, \tag{96}$$

$$\frac{dA(r)}{d\lg r} = 4\pi r^2 \times \frac{dN(r)}{d\lg r}. \tag{97}$$
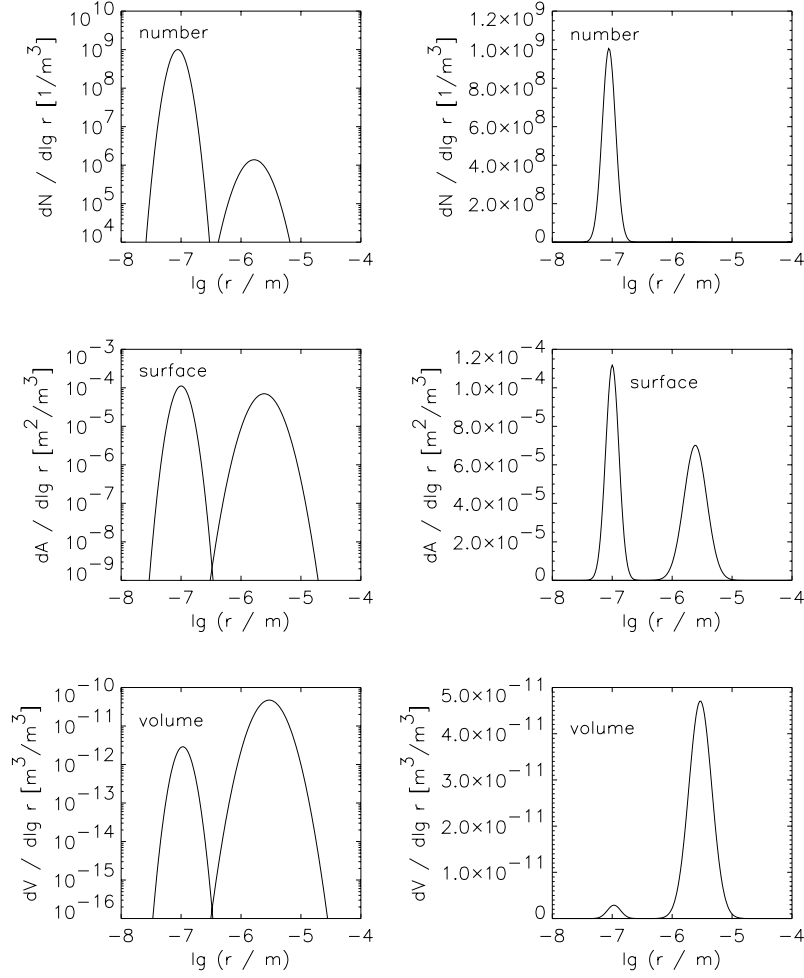
Figure 6. Typical number, surface, and volume size distributions for aerosol particles in the remote marine boundary layer. The total aerosol is the sum of two lognormal distributions for sulfate particles ($N_{tot} = 2.8 \times 10^8$ m^{-3}, $R_N = 8.8 \times 10^{-8}$ μm, $R_A = 1.0 \times 10^{-7}$ μm, $R_V = 1.1 \times 10^{-7}$ μm, $\sigma = 1.29$) and sea salt particles ($N_{tot} = 6.6 \times 10^5$ m^{-3}, $R_N = 1.7 \times 10^{-6}$ μm, $R_A = 2.4 \times 10^{-6}$ μm, $R_V = 3.0 \times 10^{-6}$ μm, $\sigma = 1.551$). Values are taken from box model calculations by Keene et al. (1998). The distributions are shown on a logarithmic scale on the left and on a linear scale on the right.

4.2. THE LOGNORMAL DISTRIBUTION

Size distributions for aerosol particles can often be parameterized using a lognormal distribution (or the sum of several lognormal distributions). The name refers to the fact that a Gaussian normal distribution results when $dN(r)/dr$ (or $dN(r)/d\lg r$)

is plotted against the logarithm of the aerosol radius. If plotted on a logarithmic y-axis, it is an upside-down parabola. The definition is:

$$\frac{\mathrm{d}N(r)}{\mathrm{d}\lg r} = \frac{N_{\text{tot}}}{\lg\sigma\sqrt{2\pi}} \times \exp\left(-\frac{(\lg r - \lg R_N)^2}{2(\lg\sigma)^2}\right). \tag{98}$$

The function contains 3 parameters: N_{tot} = total concentration of aerosol particles [m^{-3}], R_N = median radius [m], and σ = deviation around the median value [dimensionless]. The function is normalized such that integration over the entire size range from $\lg r = -\infty$ to $\lg r = +\infty$ yields N_{tot}. For $\lim\sigma \to 1$ the lognormal distribution reduces to a monodisperse distribution at radius R_N. Applying equations (96) and (97), the volume distribution $\mathrm{d}V(r)/\mathrm{d}\lg r$ and the surface distribution $\mathrm{d}A(r)/\mathrm{d}\lg r$ are obtained:

$$\frac{\mathrm{d}V(r)}{\mathrm{d}\lg r} = \frac{4\pi}{3}r^3 \times \frac{N_{\text{tot}}}{\lg\sigma\sqrt{2\pi}} \times \exp\left(-\frac{(\lg r - \lg R_N)^2}{2(\lg\sigma)^2}\right), \tag{99}$$

$$\frac{\mathrm{d}A(r)}{\mathrm{d}\lg r} = 4\pi r^2 \times \frac{N_{\text{tot}}}{\lg\sigma\sqrt{2\pi}} \times \exp\left(-\frac{(\lg r - \lg R_N)^2}{2(\lg\sigma)^2}\right). \tag{100}$$

The total aerosol volume L and the total aerosol surface A_{tot} are given by:

$$L = \int_0^\infty \left(\frac{\mathrm{d}V(r)}{\mathrm{d}r}\right)\mathrm{d}r = \int_{-\infty}^{+\infty} \left(\frac{\mathrm{d}V(r)}{\mathrm{d}\lg r}\right)\mathrm{d}\lg r, \tag{101}$$

$$A_{\text{tot}} = \int_0^\infty \left(\frac{\mathrm{d}A(r)}{\mathrm{d}r}\right)\mathrm{d}r = \int_{-\infty}^{+\infty} \left(\frac{\mathrm{d}A(r)}{\mathrm{d}\lg r}\right)\mathrm{d}\lg r. \tag{102}$$

In analogy to N_{tot} and A_{tot}, the total aerosol volume could be called V_{tot}. However, it is customary to call it the liquid water content and use the symbol L. Like the number distribution $\mathrm{d}N(r)/\mathrm{d}\lg r$, volume and surface are also lognormally distributed. This can be seen more clearly when the above functions are rearranged in order to incorporate the factors $(4\pi r^3/3)$ and $(4\pi r^2)$ into the exponential term. This yields:

$$\frac{\mathrm{d}V(r)}{\mathrm{d}\lg r} = \frac{L}{\lg\sigma\sqrt{2\pi}} \times \exp\left(-\frac{(\lg r - \lg R_V)^2}{2(\lg\sigma)^2}\right), \tag{103}$$

$$\frac{\mathrm{d}A(r)}{\mathrm{d}\lg r} = \frac{A_{\text{tot}}}{\lg\sigma\sqrt{2\pi}} \times \exp\left(-\frac{(\lg r - \lg R_A)^2}{2(\lg\sigma)^2}\right). \tag{104}$$

Here, the following definitions were used:

$$L = \frac{4\pi}{3}R_N^3 N_{\text{tot}} \times \exp\left(\frac{9(\lg\sigma)^2}{2(\lg e)^2}\right), \tag{105}$$

$$A_{\text{tot}} = 4\pi R_N^2 N_{\text{tot}} \times \exp\left(\frac{4(\lg\sigma)^2}{2(\lg e)^2}\right), \tag{106}$$

$$\lg R_V = \lg R_N + \frac{3(\lg\sigma)^2}{\lg e}, \tag{107}$$

$$\lg R_A = \lg R_N + \frac{2(\lg\sigma)^2}{\lg e}. \tag{108}$$

Lognormal parameterizations of aerosols can be found in Jaenicke (1987) and Seinfeld and Pandis (1998). As an example, the size distribution for aerosol in the remote marine boundary layer is shown in Figure 6. Marine aerosol consists mainly of small sulfate and large sea-salt particles. A separate lognormal distribution is used for each. The plots visualize several interesting features of these size distributions. Sulfate and sea-salt particles have about the same surface area. However, sulfate particles clearly dominate the number distribution, and the sea-salt particles almost exclusively determine the total aerosol volume. The number, surface, and volume distributions peak at different radii: $R_N \leq R_A \leq R_V$. They are only equal for monodisperse aerosol ($\sigma = 1$). Equations (107) and (108) can be used to convert between these radii. R_V is the *median* aerosol volume: 50 % of the total aerosol volume is in particles $r < R_V$, and 50 % in particles $r > R_V$. R_V is *not* the mean particle volume, i.e. $L \neq 4\pi/3\, R_V^3 N_{\text{tot}}$ (unless $\sigma = 1$). To calculate the liquid water content, Equation (105) must be used.

4.3. THE EFFECT OF SIZE DISTRIBUTIONS ON MASS TRANSPORT PROCESSES

The usual motivation for studying cloud/aerosol chemistry is to see how it affects the concentrations of species in the gas phase. In Section 3 expressions were developed to calculate changes in the aqueous-phase concentrations. The rate constants for gas-phase diffusion and interfacial mass transport were found to be k_{dg} and k_{i}, respectively, as defined in equations (55) and (66). In the absence of mass transfer limitations, the rate constant for aqueous-phase reactions is k_{a}. According to Equation (88), the concentration change in the aqueous phase must be multiplied with the liquid water content in order to get the concentration change in the gas phase. For a monodisperse population at radius r, the liquid water content can easily be incorporated into the rate constants:

$$Lk_{\text{dg}} = N_{\text{tot}} \times \frac{4}{3}\pi r^3 \times \frac{3D_{\text{g}}}{r^2} = N_{\text{tot}} \times 4\pi r D_{\text{g}} \propto r, \tag{109}$$

$$Lk_{\text{i}} = N_{\text{tot}} \times \frac{4}{3}\pi r^3 \times \frac{3\bar{v}\alpha}{4r} = N_{\text{tot}} \times \pi r^2 \bar{v}\alpha \propto r^2, \tag{110}$$

$$Lk_{\text{a}} = N_{\text{tot}} \times \frac{4}{3}\pi r^3 \times k_{\text{a}} \propto r^3. \tag{111}$$

These equations show how the rates of the different processes depend on the particle properties. Of course, the effect of heterogeneous chemistry is proportional to N_{tot}.

When the phases are in equilibrium, the overall rate will be determined by Lk_a, which is proportional to r^3, i.e. to the volume of the particles. If interfacial mass transport is the rate limiting step, the overall rate will be determined by Lk_i, which is proportional to r^2, i.e. to the surface area of the particles. Finally, under gas-phase diffusion limitations, the overall rate is proportional to r. When k_{mt} is influenced by both k_{dg} and k_i (cf. Figure 4), there is no simple proportionality to a function of r anymore.

To consider particles of different sizes, it is necessary to average k_{mt} over the entire size range:

$$L\bar{k}_{mt} = \int_0^\infty \left(\frac{dV(r)}{dr} \times k_{mt}(r) \right) dr, \tag{112}$$

$$= \int_0^\infty \left(\frac{4}{3}\pi r^3 \frac{dN(r)}{dr} \times \left(\frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha} \right)^{-1} \right) dr. \tag{113}$$

The mean transfer coefficient $\bar{k}_{mt}$ can be used to calculate the loss of gas-phase species to a spectrum of droplets:

$$\frac{dc_g}{dt} = -L\bar{k}_{mt} \left(c_{g,\infty} - \frac{c_{a,surf}}{k_H^{cc}} \right). \tag{114}$$

This parametrization works fine for species where the aqueous-phase concentration $c_{a,surf}$ is equal for droplets of all sizes. Otherwise the process of mass transfer to droplets of different sizes must be calculated explicitly for all size categories. In addition, it might be necessary to calculate the chemistry of two same-sized particles separately if their chemical composition is different. This is the case when the aerosol population is externally mixed.

5. Conclusions

The interactions between gas-phase species and liquid cloud/aerosol particles have been reviewed. Under equilibrium conditions, Henry's law applies. Kinetic expressions describing the mass transport between the phases were compared. Some interesting facts that follow directly from previously published papers but were not explicitly stated there, are:

-   There are many ways to define k_H. Describing the aqueous phase in terms of molality seems to be the best choice, especially when the effects of temperature and of other solutes are considered.
-   Aqueous-phase diffusion does not limit the overall reaction rate at very high aqueous-phase reaction rates.
-   For species of low solubility, the dimensionless Henry's law coefficient k_H^{cc} serves as an upper limit of the accommodation coefficient: $\alpha \le k_H^{cc}$

—   The difference between the mass transfer coefficients developed by Fuchs and Sutugin (1971) and Schwartz (1986) is small. The advantage of the latter is its simplicity.

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