

GUIDE TO USE OF DATASHEETS FOR HETEROGENEOUS PROCESSES

IUPAC Subcommittee for Gas Kinetic Data Evaluation

1. Introduction

Heterogeneous processes considered in this evaluation involve chemical and /or physical interactions between trace gases and atmospheric condensed phase material. Broadly this material falls into 3 categories: (i) large water droplets (diameter, $d > 1 \mu\text{m}$), (ii) fine liquid submicron ($d < 1 \mu\text{m}$) aerosol particles, and (iii) solid aerosol particles (coarse, fine, ultrafine mode). The interaction can be reversible (physisorption or dissolution), reactive, catalytic or a combination of all or some of these operating in parallel or sequentially, and can depend strongly on ambient conditions such as e.g. temperature or relative humidity. Atmospheric aerosols vary greatly in composition and include aqueous droplets, such as water, salt solutions (e.g., halide and sulphate), sulphuric acid, semi volatile organics, and solid particles, such as ice, acid hydrates, soot, mineral dust, or salts. Solid particles may be coated with aqueous films; aqueous particles may include insoluble material as a separate phase or in the form of a coating.

The parameterisation of a heterogeneous process depends on the nature of the surface. A proper description of the interaction of a trace gas with a surface would include transport to and accommodation at the surface, followed by a number of competitive or parallel processes such as desorption back to the gas phase, reaction with the substrate surface or with other trace gases on the surface, and diffusion into and reaction in the particle bulk (important for liquid aerosol; less so for solid particles). The rates and efficiencies of these processes are controlled by surface and bulk-phase rate coefficients, local reactant concentrations, diffusion coefficients in the condensed phase, and solubilities. Each of these controlling factors may change with temperature and composition. Atmospheric heterogeneous processes can be highly complex.

Only rarely are all the individual steps controlling reaction rates of heterogeneous processes known. A quasi steady state resistance model has frequently been used to

describe the uptake of gas species to surfaces, and to relate the experimentally observable net probability of uptake (γ , see below) to the physical parameters that control it. In this model a linear combination of flux resistances (decoupled and normalized fluxes) by analogy to resistances in electric circuits, is used to describe the uptake process (Jayne et al., 1990; Hanson, 1997; Ammann et al., 2003; Pöschl et al., 2007), and we will refer to these formulations below where appropriate. Models involving solution of coupled differential rate equations of mass transport and chemical reactions using continuum flow formulations (Winkler et al., 2004) and gas kinetic formulations (Flückiger and Rossi, 2003; Behr et al., 2004; Pöschl et al., 2007) have recently been described.

Experiments are usually carried out in regimes in which the process of interest is limiting (i.e. the slowest step in the overall process). However, only a systematic variation of conditions will reveal the identity of this slowest elementary step.

2. Description of heterogeneous kinetics

2.1. Definition of the uptake coefficient

The most widely used approach to describe the kinetics of heterogeneous processes is to use the uptake coefficient, γ , which is the *net* probability that a molecule X undergoing a gas-kinetic collision with a surface is actually taken up at the surface. This approach links the processes at the interface and beyond with an apparent first order loss of X from the gas phase:

$$\frac{d[X]_g}{dt} = -k_p[X]_g = -\gamma \frac{\bar{c}}{4} [SS]_g [X]_g \quad (1).$$

$[X]_g$ denotes the concentration of X in the gas phase (molecule cm^{-3}), $[SS]_g$ is the specific surface area of the condensed phase (cm^{-1}) (i.e., surface area of condensed phase per volume of gas phase), and \bar{c} is the mean thermal velocity of X (cm s^{-1}). γ often depends on time, as uptake may be limited by adsorption equilibrium on the surface, by a limited number of reactants on the surface, by solubility, or by a limited number of reactants in the bulk of the particles. γ may also depend on the gas phase concentration of X. Therefore, γ is not a constant, and γ values reported from laboratory measurements often

cannot be transferred directly to other conditions. This must be done through a proper parameterization of the processes at the interface and beyond, as outlined below.

2.2. Gas phase diffusion

If γ is large, $[X]_g$ may become depleted near the particle surface. In this case, a correction factor is commonly applied, such that equation (1) can still be used to relate the net flux into the particle phase with the overall loss from the gas phase. γ in equation (1) is then replaced by γ_{eff} , which is given by $\gamma_{\text{eff}} = C_{\text{diff}} \gamma$, where C_{diff} is a correction factor. Under appropriate steady state assumptions, this relation can also be expressed in the form of a resistor formulation (Schwartz, 1986; Hanson and Ravishankara, 1994; Finlayson-Pitts and Pitts, 2000):

$$\frac{1}{\gamma_{\text{eff}}} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\gamma_{\text{net}}} \quad (2)$$

Approximate formulas for C_{diff} or Γ_{diff} have been derived in the literature (Fuchs and Sutugin, 1970; Brown, 1978; Seinfeld and Pandis, 1998) for various geometries, such as suspended aerosol particles, but also cylindrical flow tubes. They are a function of the geometry (e.g., particle diameter, d_p) and the diffusion coefficient of X, D_g , and γ . Therefore, temperature and bath gas dependent diffusion coefficients for X are required. Diffusion control may also limit uptake rates to particles in the atmosphere, requiring a similar treatment for uptake kinetics.

2.3. Surface accommodation and kinetics of adsorption

A molecule colliding with the surface of solid or liquid condensed matter can undergo elastic or inelastic scattering processes that involve collisions with one or a few surface atoms or molecules on time scales of up to 10^{-12} s. Elastic and inelastic scattering result in reflection back to the gas phase. The molecule can also undergo adsorption, in which case it accommodates into a weakly bound state, which may involve hydrogen bonds, charge transfer, or Van der Waals interactions. Adsorbed molecules may leave the surface through thermally activated desorption, which results in lifetimes on the surface of typically between nanoseconds and seconds at atmospheric temperatures. Thermally desorbing or scattered molecules can be distinguished through molecular beam

experiments (Nathanson et al., 1996; Morris et al., 2000). The adsorption state as defined above is usually referred to as physisorption in the surface science literature (Masel, 1996). Physisorption should be differentiated from chemisorption which involves breaking of chemical bonds or significant distortion of electronic structure of adsorbate and substrate. As discussed below, chemisorption is considered to be a surface reaction. We recommend use of the term "surface accommodation coefficient", α_s , for the probability of adsorption on a clean surface. Note that the symbol S and terms such as sticking probability or adsorption coefficient are used in the literature (Tabazadeh and Turco, 1993; Davidovits et al., 1995; Carslaw and Peter, 1997; Hanson, 1997; Ammann et al., 2003; Pöschl et al., 2007), however often these terms lack an unequivocal definition. The term thermal accommodation coefficient, α_t , has been used to describe the probability that a molecule accommodates to the thermal energy of the substrate upon adsorption in a single collision model, when a molecule collides with the surface (Li et al., 2001; Worsnop et al., 2002).

The concept of Langmuir type adsorption assumes that molecules can only adsorb on free surface sites, so that the rate of adsorption ($\text{cm}^{-2} \text{s}^{-1}$) is given by

$$J_{\text{ads}} = \alpha_s \frac{\bar{c}}{4} (1 - \theta) [X]_{\text{g}} \quad (3)$$

θ denotes the fractional surface coverage, which is related to the surface concentration, $[X]_{\text{s}}$, via $[X]_{\text{s}} = \theta N_{\text{max}}$, where N_{max} is the maximum number of available surface sites per cm^2 . The reverse process, thermally activated desorption, is usually parameterised by a first order rate expression:

$$J_{\text{des}} = k_{\text{des}} [X]_{\text{s}} \quad (4)$$

k_{des} denotes the desorption rate constant (s^{-1}). In the absence of surface reaction or transfer to the bulk, the uptake coefficient as a function of time is given by

$$\gamma(t) = \alpha_s e^{-Bt} \text{ with } B = \alpha_s \frac{\bar{c} [X]_{\text{g}}}{4 N_{\text{max}}} + k_{\text{des}} \quad (5)$$

Equation (5) indicates that for low coverages, where $k_{\text{des}} \gg \alpha_s \bar{c} [X]_{\text{g}} / 4 N_{\text{max}}$ (relevant for most atmospherically relevant adsorption processes), the characteristic time to reach equilibrium is given by $1/k_{\text{des}}$. After equilibrium has been established (see below), γ drops to zero. Therefore, at all concentrations, very high time resolution is necessary to observe

an uptake coefficient equal to α_S , and laboratory experiments have to be carefully evaluated to judge whether initial uptake coefficients (reported as γ_0) may correspond to α_S . In the data sheets we tabulate reported values of γ_0 and provide a preferred value for α_S if appropriate and as discussed in the associated comments. Equation (5) may also be used to parameterise the temperature dependence of the uptake coefficient observed at a given time or averaged over a given time interval.

2.4. Adsorption equilibrium

The kinetics of adsorption may be relevant for extracting α_S from laboratory measurements, but only rarely represents a rate limiting step of loss of gas phase species under atmospheric conditions. Here, adsorption equilibrium is of wider importance as it may be used to estimate gas surface partitioning (e.g., in ice clouds) or because it defines the concentration of surface species available for surface reaction or for transfer to the bulk underneath (see below). Most of the relevant literature on adsorption equilibria covers trace gases interacting with ice and, to a lesser degree, mineral dust. However, adsorption of surface active gases on aqueous solutions has been described using the same concept. Adsorption equilibrium is established when $J_{\text{ads}} = J_{\text{des}}$ and can be described by

$$\theta = \frac{K_{\text{LangC}} [X]_g}{1 + K_{\text{LangC}} [X]_g} \quad (6)$$

$$K_{\text{LangC}} = \frac{\alpha_S \bar{c}}{4k_{\text{des}} N_{\text{max}}} \quad (7)$$

Equation (6) is an isotherm commonly referred to as the Langmuir isotherm, which allows derivation of the partition coefficient, K_{LangC} , from measurements of surface coverage (molecule cm^{-2}) as a function of trace gas concentration or pressure. Equation (7) also relates the partition coefficient to the kinetic parameters that determine the equilibrium on a molecular level. Therefore, measurement of K_{LangC} also provides constraints on α_S .

Note that this isotherm only holds for the case that the adsorbing species compete for fixed surface lattice sites and within the assumptions of the simple picture described

above in the context of adsorption kinetics. However, it appears to be a reasonable approximation for adsorption characteristics on model surfaces used in laboratory studies of adsorption to solid surfaces (except on ice surfaces when adsorption of some trace gases leads to hydrate formation or surface melting) and of insoluble gases on liquid surfaces. We have adopted this formalism for representation of evaluated data, unless there is a gross departure from the simple picture. Note also that an expression similar to that of equation (6) can be used to express the equilibrium between the bulk of e.g. an aqueous solution and the surface for surface active solutes (Donaldson, 1999).

From a thermodynamic point of view, the equilibrium between the gas and the surface can also be expressed by using a dimensionless partition coefficient, K :

$$\frac{[X]_s}{[X]_g} \times \frac{A}{V} = \exp\left(\frac{\Delta G_{\text{ads}}^0}{RT}\right) \equiv K \quad (8)$$

where A/V is the area-to-volume ratio (cm^{-1}) of an ideal gas adsorbed at the surface ($\sim 1.7 \times 10^7 \text{ cm}^{-1}$; (Kemball, 1946; Kemball and Rideal, 1946)) and ΔG_{ads}^0 is the free energy of adsorption. A/V defines the standard state for the adsorbed phase, which corresponds to a molar area of $3.74 \times 10^{-7} \text{ m}^2\text{mol}^{-1}$. ΔG_{ads}^0 is related as usual via the Gibbs equation to the enthalpy and entropy of adsorption:

$$-RT \ln K = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0 \quad (9)$$

The relation between K and K_{LangC} (the ‘‘C’’ of LangC refers to the fact that units of concentration in molecules cm^{-3} are used) is equivalent to

$$K_{\text{LangC}} = K \cdot \frac{V}{A} \cdot \frac{1}{N_{\text{max}}} \text{ in units of } \text{cm}^3 \text{ molecule}^{-1} \quad (10)$$

The use of gas pressures results in:

$$K_{\text{LangP}} = K \cdot \frac{V}{A} \cdot \frac{1}{k_{\text{B}}TN_{\text{max}}} \text{ in units of } \text{Pa}^{-1} \text{ or } \text{atm}^{-1} \text{ or } \text{Torr}^{-1} \text{ or } \text{mbar}^{-1} \quad (11)$$

A modified analysis using only the linear regime of the adsorption isotherm is sometimes possible. The partition coefficient (K_{linC}) once again has different units:

$$K_{\text{linC}} = K \cdot \frac{V}{A} \quad (12)$$

K_{linC} has units of molecule cm^{-2} / molecule cm^{-3} (or cm) if concentrations (in molecule cm^{-3}) are used, and units of molecule $\text{cm}^{-2} \text{Pa}^{-1}$ or molecule $\text{cm}^{-2} \text{Torr}^{-1}$ if pressure is used.

Fractional surface coverages can be calculated from each different form of the partition coefficient via:

$$\theta_X = K_p^0 \frac{V}{A} \frac{p_X}{k_B T N_{\text{max}}} = K_p^0 \frac{V}{A} \frac{[X_g]}{N_{\text{max}}} = K_{\text{linC}} \frac{[X_g]}{N_{\text{max}}} = K_{\text{linP}} \frac{p_X}{k_B T N_{\text{max}}} = K_{\text{LangC}} [X_g] = K_{\text{LangP}} p_X \quad (13)$$

For the purpose of comparing partition coefficients and deriving preferred expressions for calculating equilibrium surface coverages, a single form of the partition coefficient is required. In principle, K , would be the best choice; the disadvantage is that it is difficult to extract from the various studies, if experimental surface to volume ratios ($S_{\text{exp}}/V_{\text{exp}}$) are not known, or if N_{max} has to be chosen arbitrarily and not from the experiment itself. Therefore, for practical purposes (e.g., using the constants to calculate coverages) reporting consistently in the form of K_{linC} has the advantage that no inherent assumption about N_{max} has to be made to derive partitioning from the experiments at low pressures. The tabulated values of partition coefficients are therefore presented as K_{linC} . The accompanying notes in each data sheet provide the original expressions and the values of N_{max} and V/A used to calculate K_{linC} .

K_{linC} can be calculated from other forms of the partitioning coefficient as shown below:

Convert from	To	Multiply by
$K_{\text{LangC}} (\text{cm}^3)$ or $K_{\text{LangP}} (1/\text{Pressure})$	$K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$ $K_{\text{linP}} (1/\text{Pressure})$	N_{max}
$K_{\text{LangP}} (\text{Pa}^{-1})$	$K_{\text{LangC}} (\text{cm}^3)$	

or $K_{\text{linP}} (\text{cm}^{-2} \text{ Pa}^{-1})$	$K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$	$1.381 \times 10^{-17} T$
$K_{\text{LangP}} (\text{mbar}^{-1})$ or $K_{\text{linP}} (\text{cm}^{-2} \text{ mbar}^{-1})$	$K_{\text{LangC}} (\text{cm}^3)$ $K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$	$1.381 \times 10^{-19} T$
$K_{\text{LangP}} (\text{bar}^{-1})$ or $K_{\text{linP}} (\text{cm}^{-2} \text{ bar}^{-1})$	$K_{\text{LangC}} (\text{cm}^3)$ $K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$	$1.381 \times 10^{-22} T^a$
$K_{\text{LangP}} (\text{Torr}^{-1})$ or $K_{\text{linP}} (\text{cm}^{-2} \text{ Torr}^{-1})$	$K_{\text{LangC}} (\text{cm}^3)$ $K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$	$1.036 \times 10^{-19} T$
K	$K_{\text{linC}} (\text{cm}^{-2} / \text{cm}^{-3})$	V/A

If data are available from the low coverage (linear) part of the isotherm these are used preferably as the influence of lateral interactions is reduced, and N_{max} , which is often difficult to obtain experimentally due to adsorbate-adsorbate interactions (Jedlovsky et al, 2006), is not required. The Van't Hoff equation (i.e., the differential form of the Gibbs equation):

$$\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H^o}{R} \quad (14)$$

describes the temperature dependence of K , but the entropy and enthalpy of adsorption derived from this analysis can be coverage dependent and this needs to be considered when comparing results from different experiments.

In cases where the adsorbing molecule dissociates upon adsorption onto a solid-like surface the Langmuir isotherm takes a modified form:

$$\theta = \frac{N}{N_{\text{max}}} = \frac{\sqrt{K_{\text{Lang}} [X]}}{1 + \sqrt{K_{\text{Lang}} [X]}} \quad (15)$$

The occupancy of two adjacent surface sites for accommodation leads to a square root dependence of surface coverage at low $[X]$, which can be used as a diagnostic for

dissociative adsorption. This is however rarely unambiguously observed experimentally for atmospheric surfaces

2.5. Surface reactions

Parameterisation of uptake resulting from reaction of trace gases on a surface (reactive uptake) requires knowledge of the mechanism of the reaction. Generally there are two types of reaction. First, those in which the molecule arriving at the surface reacts with a constituent of the bulk phase (usually water molecules) to form either involatile products (e.g., stable hydrates) or volatile products which partition back to the gas phase. Second, those in which the molecule arriving at the surface reacts with a second species which is present on the surface in the adsorbed state to form either involatile or volatile products. In both types the kinetics depend on the surface concentration of the second reactant, which must be included in any parameterisation of the reactive uptake coefficient. The two mechanisms, which are commonly used to describe the kinetics of surface reactions, are often referred to as Langmuir-Hinshelwood (LH) and Eley-Rideal mechanisms (ER). It should be noted that some reports in the literature use the term Langmuir-Rideal for the latter and that the reverse abbreviation RE has also been used (see also IUPAC Gold Book). They differ in that the former involves adsorption of the arriving molecule at available surface sites prior to a bimolecular reaction. The second involves direct collision induced reaction of the arriving gaseous molecule with a reactant molecule on the surface. The LH mechanism thus may involve competition of both reactant molecules for available surface sites. For parameterisation of the uptake coefficients we adopt the approach presented by Ammann et al. (Ammann et al., 2003), which builds on earlier studies (Elliott et al., 1991; Mozurkewich, 1993; Tabazadeh and Turco, 1993; Carslaw and Peter, 1997).

Bimolecular reaction between two surface species

The parameterisation for the reactive uptake coefficient, γ , for gas phase species X reacting with surface species, Y, after adsorption on the surface (LH type mechanism) is given by:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s} \quad \text{with} \quad \Gamma_s = \frac{4k_s[Y]_s K_{LangC}(X)N_{\max}}{\bar{c}(1 + K_{LangC}(X)[X]_g)} \quad (16)$$

Here $[Y]_s$ the surface concentration (molecules cm^{-2}) of species Y and k_s the surface reaction rate coefficient (units of $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$). $1/\Gamma_s$ can be considered the resistance for the surface reaction. Note that Γ_s represents a normalized rate and is therefore not restricted to values smaller than one. If Y is a volatile molecule also present in the gas phase, its equilibrium surface concentration, $[Y]_s$ can be calculated using an appropriate adsorption isotherm. Values of $k_s K_{LangC}(X)$ can be determined experimentally from measurements of γ , as a function of surface coverage $[Y]_s$. Equation (16) demonstrates that γ depends on the gas phase concentration of X, if $K_{LangC}(X)[X]_g$ is similar to or larger than 1 (i.e., at high coverage). This is especially important when interpreting data from laboratory experiments performed using gas-phase reactant concentrations which lead to significant surface coverage. In the data sheets, we provide preferred values for α_s and k_s .

Direct gas – surface reaction

Parameterisation for the reactive uptake coefficient, γ , for gas phase species X directly reacting with surface species, Y, upon collision (ER type mechanism) is given by:

$$\gamma = \gamma_{gs} = \frac{\gamma_{gs}(X)[Y]_s}{N_{\max}(Y)} = \gamma_{gs}(X)\theta(Y) \quad (17)$$

Here γ_{gs} is the elementary reaction probability that a gas phase molecule X colliding with surface component Y reacts with it. $N_{\max}(Y)$ denotes the maximum coverage of Y for a volatile species Y in equilibrium with the gas phase. γ can be calculated for a given gas

phase concentration of Y if values of $K_{\text{LangC}}(\text{Y})$ and γ_{gs} are available. In absence of other rate limiting reactions, values of γ_{gs} can be determined experimentally from measurements of γ as a function of surface coverage near saturation, or by extrapolation using an appropriate adsorption isotherm. In the ER type mechanism, γ does not depend on the gas phase concentration of X, whereas in the LH type mechanism (at high [X]) it does. Also the temperature dependence, driven by the temperature dependence of $K_{\text{LangC}}(\text{X})$ in the LH case, is substantially different.

2.6. Exchange with the bulk and bulk accommodation

Previously, the process of transfer of a gas molecule from the gas phase into the bulk has been considered a quasi-elementary process, and the mass accommodation coefficient has been defined as the probability that a molecule colliding with the surface is actually taken up into the bulk, mostly in relation with liquids. However, in many cases it is necessary to decouple this process into adsorption on the surface and surface to bulk transfer, i.e., dissolution (Davidovits et al., 1995; Hanson, 1997).

With the aim to clearly differentiate uptake into the bulk from surface accommodation, the term ‘bulk accommodation’ is recommended, and the corresponding coefficient as bulk accommodation coefficient, α_{b} . In the absence of surface reactions,

$$\alpha_{\text{b}} = \alpha_{\text{s}} \frac{k_{\text{sb}}}{k_{\text{sb}} + k_{\text{des}}} \quad (18)$$

In equation (18), k_{sb} denotes the surface to bulk transfer rate coefficient in units of s^{-1} . If the adsorption equilibrium is established much faster than transfer to the bulk, the two processes can be expressed in the form of separated resistances:

$$\frac{1}{\alpha_{\text{b}}} = \frac{1}{\alpha_{\text{s}}} + \frac{1}{\Gamma_{\text{sb}}} \quad \text{with} \quad \Gamma_{\text{sb}} = \frac{\alpha_{\text{s}} k_{\text{sb}}}{k_{\text{des}}} \quad (19)$$

Equations (18) and (19) also allow parameterization of the temperature dependence of α_{b} , which has been used as a proof of the nature of bulk accommodation as a coupled process (Davidovits et al., 1995).

2.7. Solubility limited uptake into the bulk

In the absence of surface or bulk reactions, uptake into the bulk of liquid particles proceeds until the solubility is reached. Under quasi-steady state conditions, the uptake coefficient can be described by

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{sol}}} \quad \text{with} \quad \Gamma_{\text{sol}} = \frac{4 \cdot HRT}{\bar{c} \cdot \sqrt{\pi}} \cdot \sqrt{\frac{D_l}{t}} \quad (20)$$

H denotes the Henry's Law coefficient (M atm^{-1}), R the gas constant ($1 \text{ atm mol}^{-1} \text{ K}^{-1}$) and D_l the liquid phase diffusion coefficient (cm^2s^{-1}) (Schwartz, 1986). Solubility limited uptake can be used to measure the product $H(D_l)^{0.5}$, through the time dependence of the observed γ .

2.8. Reactive uptake into the bulk

For trace gas uptake to the bulk of liquid (usually aqueous) particles,

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_b} \quad \text{with} \quad \Gamma_b = \frac{4HRT}{\bar{c}} \sqrt{D_l \cdot k_{\text{rxn}}^1} \quad (21)$$

k_{rxn}^1 is the pseudo first order rate coefficient for reaction of species taken up into the bulk. For small droplets the concept of the diffuso-reactive length is important. This is the average distance beyond the surface of the particle in which reactions take place and is given by:

$$l = \sqrt{\frac{D_l}{k_{\text{rxn}}^1}} \quad (22)$$

For spherical particles, equation (21) can be modified to account for this with:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{\bar{c}}{4HRT \sqrt{D_l \cdot k_{\text{rxn}}^1} \left[\coth\left(\frac{r}{l}\right) - \left(\frac{l}{r}\right) \right]} \quad (23)$$

This is the basis of the "Framework" paper (Hanson et al., 1994) for modelling uptake rates to stratospheric aerosol. Note that for a molecule that can dissociate in the aqueous phase, an effective solubility, H^* , is used whereby:

$$H^* = H \times \left(\frac{1 + K_{\text{diss}} [\text{H}^+]_e}{K_w} \right) \quad (24)$$

K_w is the autoprotolysis constant of H_2O , K_{diss} is the acid dissociation constant of the trace gas in water and $[\text{H}^+]_e$ is the equilibrium hydrogen ion concentration at the droplet surface.

2.9. Coupled processes on the surface and in the bulk

When processes occur on both the surface and in the bulk, adsorption and transfer to the bulk have to be separated. Following (Jayne et al., 1990; Davidovits et al., 1995; Hanson, 1997; Shi et al., 1999; Ammann et al., 2003; Pöschl et al., 2007), coupling a Langmuir-Hinshelwood type surface reaction with a reaction in the bulk leads to

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \frac{1}{\frac{1}{\Gamma_{sb}} + \frac{1}{\Gamma_b}}} \quad (25)$$

In the case of an Eley-Rideal reaction which occurs without prior adsorption or surface to bulk transfer, the resistance acts in parallel to adsorption, leading to an expression proposed by (Pöschl et al., 2007):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{gs} + \frac{1}{\frac{1}{\alpha_s} + \frac{1}{\Gamma_{sb}} + \frac{1}{\Gamma_b}}} \quad (26)$$

Note that while the expression (26) is consistent with the resistor diagram suggested by Hu et al. (1995), it is not consistent with their suggested expression for γ . While they mentioned a Eley-Rideal mechanism, their parameterisation is not consistent with either

of the two expressions. In follow-up papers (e.g., Shi et al., 1999) they used expression (25) as well.

3. Surface types considered

3.1. SOLID SURFACES

3.1.1. Ice

Experimental ice films are either single crystal or polycrystalline and can vary greatly in surface morphology, depending on the mode of formation (vapour deposition versus frozen solutions) and number of grain boundaries / triple points, which may contain supercooled water. This leads to significant uncertainty in the effective surface area of the ice films. There has also been much discussion about the role of pore diffusion (Keyser et al., 1991; Hanson and Ravishankara, 1993; Keyser and Leu, 1993; Leu et al., 1997) in vapour deposited ice films (see also below). Its importance depends on both the properties of the adsorbing species as well as on the condensed phase. For these reasons, when evaluating measurements of trace gas uptake to ice films we always cite the mode of formation of the ice film and any relevant information regarding surface morphology (e.g. BET surface areas).

In addition, there have been many experimental studies of trace gas-ice interaction but many were carried out under experimental conditions (temperature and trace gas partial pressure) that correspond to stability regions of the phase diagram for either hydrate formation or supercooled aqueous solutions, so that the surface cannot be considered as “ice”. It has been found that the interaction of a trace gas with an ice film made from slowly freezing an aqueous sample can, to a good approximation, be described by the geometric surface area. Evidence is provided by BET surface measurements and by the fact that many molecules that react weakly have similar values of N_{\max} , and that these values are very close to theoretical calculations (Abbatt, 2003).

3.1.2. NAT (nitric acid trihydrate), NAD (nitric acid dihydrate) and SAT (sulfuric acid tetrahydrate)

Conditions in the stratosphere can be thermodynamically favourable for the existence of solid particles consisting of stable hydrates of nitric, hydrochloric and sulphuric acid.

Uptake studies have mainly concentrated on nitric acid-trihydrate (NAT), nitric acid-dihydrate (NAD) and sulphuric acid tetrahydrate (SAT) . Films or particles of these substrates are prepared in similar fashion to ice films by freezing mixtures or co-deposition of acid and water from the vapour phase. The films have similar physical properties to pure ice films but the surface character depends on RH in a different way to ice as a result of differences in water vapour pressure. For each stoichiometric crystalline acid hydrate there is a water-rich and a water-poor region on each side of the solidus/liquidus curve. The characterization of the water activity in the neighboring regions on the solidus/liquidus curve is important in view of the dependence of many hydrolysis reactions on water activity.

3.1.3. Mineral Oxides

Investigations of trace gas uptake to mineral oxide surfaces, include naturally occurring “dust” from e.g. Saharan or Asian source regions and surrogate materials including CaCO_3 , Al_2O_3 , Fe_2O_3 , MgO and clay minerals such as kaolinite, illite etc., which are components of atmospheric dust. The mineral oxides are often present as bulk, porous samples in laboratory experiments, which requires careful analysis to take into account interstitial surface areas. The comparison of results from different studies is often difficult due to the use of different substrates (e.g. mineralogically distinct “natural dust” samples) and different modes of sample presentation and models for surface area calculation (see below). Recognizing that synthetic oxides do not necessarily mimic the reactivity of natural dust, our preferred values are presently based on experiments using Saharan or Asian dust samples, preferably presented in aerosol form. For some trace gases, both the uptake coefficient and adsorption capacity of some dust surfaces are found to have a strong dependence on humidity.

3.1.4. Soot

Soot is formed in hydrocarbon flames and consists of insoluble elemental carbon (EC, or black carbon, BC) and a soluble organic fraction (OC) that may reach up to 50% by weight of the soot. The structure of soot is composed of spherical primary particles of 3 to 15 nm that agglomerate to chain aggregates of widely varying dimension (50 nm to

several μm) whose fractal dimension usually is slightly less than two. Pore diffusion theory most likely cannot be applied to bulk soot owing to the non-uniformity and variable geometry of the interstitial space between the primary particles making up the agglomerates.

The reactivity of soot and the products of heterogeneous reaction depend to a large extent on the combustion conditions during soot production (Gerecke et al., 1998; Stadler and Rossi, 2000; Arens et al., 2001) together with other parameters. The soots most commonly used in laboratory investigations are amorphous or black carbon because they have been well characterized (for instance Degussa soot), soot generated from an arcing graphite electrode, hydrocarbon flame soot and soot formed in internal combustion engines (cars) or gas turbine/jet engines (aircraft). These soots have different organic contents and surface properties/reactivities and it is therefore often difficult to compare experimental results.

3.1.5. Solid inorganic salt particles

At low humidity, below efflorescence RH, particles containing electrolyte acids and salts can exist as solid crystals. Examples are dry and frozen sea salt, ammonium sulphate, higher molecular weight organic acids. Bulk or aerosol substrates of solid salts with defined and reproducible surface areas are less easily prepared. However, salts are not nano- or microporous because the calculated BET surface area based on the measured average dimension of the salt crystals agrees well with the measured BET surface area (Timonen et al., 1994). Coated surface (coated wall flow system or Knudsen cell) configuration or aerosol flow tubes have been used. Control of relative humidity is an important factor in providing a reproducible surface.

3.2. LIQUID SURFACES

3.2.1. Sulfuric Acid

Stratospheric aerosols consist mainly of sub-micron size liquid particles containing aqueous concentrated H_2SO_4 (50–80 wt %) at low temperature (185–260 K). The water content depends in a predictable way on the relative humidity, which is defined by the temperature and the absolute water concentration. Substrates with well characterised

surface area and acid content are relatively straightforward to prepare, either as bulk substrates or as an aerosol of sub-micron particles of defined size distribution. The latter form minimises the limiting effects of gas-phase diffusion on the surface on the uptake rates, which can be a problem when bulk surfaces are used and γ_{net} values are large.

3.2.2. Aqueous Salts

The most common aerosols in the troposphere consist of water soluble electrolyte salts. Over marine regions the aerosol is dominated by sea salt aerosol, with NaCl as the main constituent. In continental regions ammonium sulphate, ammonium bisulphate, and ammonium nitrate are major constituents of the aerosol. The phase of the particles depends on relative humidity. At low humidity, below efflorescence RH, the particles can contain solid crystals. At higher humidity ($\geq 40\%$) the particles exist as aqueous droplets and this is the predominant form in the troposphere. Liquid substrate surfaces with well characterised surface area and electrolyte content are relatively straightforward to prepare, either as bulk substrates in wetted wall or droplet train configuration, or as an aerosol of sub-micron particles of defined size distribution.

3.2.3. Organics

There is a substantial organic content of the atmospheric aerosol. The organic composition is dominated by low volatility water soluble oxygenated VOC of very complex nature typically containing polyols, di- and poly-carboxylic acids. These organics are often present in particles of mixed inorganic/organic composition, and are usually liquid phase, but may also constitute a separate, internally mixed subphase. Some organics in the aerosol (e.g., long-chain carboxylic acids) are surfactants which may form a surface coating on the particles. The preferred experimental configuration for uptake measurements is on aerosols of sub-micron particles of defined size distribution. These can be readily prepared using solutions made up with known amounts of the components.

3.3 SURFACE AREAS

γ is usually obtained from observed loss rates of gas-phase species and calculated collision rates with the surface. For the latter the surface area available for

uptake/reaction (A) is required. For liquid surfaces this poses no problems as the surface is “smooth” at the molecular level and the geometric surface area (A_{geom}) is generally applicable and readily defined. For solid surfaces (ice, soot, dust etc.) there is a finite probability that the impinging trace gas can collide with internal surface within the time scale of determination of the uptake coefficient. This issue is especially relevant for bulk samples, such as coatings or powders, but may also apply for aerosol particles. The geometric surface area represents a lower limit to A , and an upper limit to γ_{net} is obtained. The other extreme is the use of the total sample surface area (e.g. the N_2 -BET surface area, A_{BET}) which is the maximum available surface area, including internal pore volume and bulk surface area of granular material. This is usually expressed as surface area per unit weight of solid sample, which must also be known. Use of A_{BET} yields a lower limit to γ_{net} . The surface area available to the trace gas will be determined by parameters such as its surface accommodation coefficient and its desorption lifetime, which limit the rate of diffusion into the interstitial space of a porous sample. Pore diffusion corrections have frequently been applied, both for ice and mineral dust substrates (Keyser et al., 1991; Keyser and Leu, 1993; Fenter et al., 1995; Leu et al., 1997; Michel et al., 2002; Carlos-Cuellar et al., 2003), and yield uptake coefficients, γ_{PD} that lie between γ_{geom} and γ_{BET} . The application of the geometric, or BET surface area or pore diffusion corrections leads to values of γ_{obs} that deviate sometimes by orders of magnitude, and has been the subject of much debate (Leu et al., 1997; Hanson and Ravishankara, 1993). Sample preparation and presentation may also have a significant effect on the sample surface area and hence the derived uptake coefficients. For example, ice films created by freezing liquid water may have a smaller surface area than those made by vapour deposition, and single crystal mineral oxides are often less reactive than powdered samples of the same material. The use of aerosol particles rather than bulk surfaces in principle provides a better mimic of atmospheric conditions for experimental surface area.

4. Organisation of the Datasheets

The basic structure of the heterogeneous datasheets is similar to the well established datasheets on homogeneous gas-phase reactions. For each heterogeneous interaction on a

particular substrate we give a list of experimentally measured values of the uptake coefficients and partition coefficients where appropriate for physical uptake. The parameters are distinguished according to the definitions given above (e.g. γ , γ_{ss} , K_{linC} , etc.). Also given are references and pertinent information about the technique, reactant concentration, substrate and other conditions in linked comments. Reflecting the strong influence of the choice of surface area and sample preparation on γ (see section 3) such information is, when available, also given.

Recommended values for the uptake coefficient, α_s , k_s , K_{linC} , N_{max} , and α_b are provided. Recommended temperature dependencies are given in Arrhenius form when appropriate, together with our estimate of the uncertainties in the parameters. Comments on the state of the data set and justification of the recommendations are then presented, followed by a list of references cited. The reaction ordering of reacting species within each surface category follows that adopted for gas phase reactions, i.e. Ox, HOx, NOx, SOx, organics, and halogenated species.

Table 1: Parameters used to describe heterogeneous reactions

Parameter	Description	Units	notes
γ	Net uptake coefficient	-	a
Γ_b	Limiting uptake coefficient for bulk reaction (liquid)	-	
Γ_{sol}	Limiting uptake coefficient for dissolution (liquid)	-	
Γ_{diff}	Limiting uptake coefficient for gas-phase diffusion	-	
γ^{ss}	Experimentally observed, steady state (time independent) uptake coefficient	-	
γ^0	Experimentally observed, initial uptake coefficient	-	
α_s	Surface accommodation coefficient	-	b
k_s	Surface reaction rate coefficient	$\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	
α_b	Bulk accommodation coefficient	-	c
K_{linC}	Gas-Surface partition coefficient (solid surfaces)	$\text{cm}^{-2} / \text{cm}^{-3}$	d
K_v	Gas-Volume partition coefficient (solid surfaces)	$\text{cm}^{-3} / \text{cm}^{-3}$	e
H	Solubility (Henry)	$\text{mol} / \text{l.atm}$	
D_l	Liquid phase diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$	
D_g	Gas phase diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$	

Notes

- a: As γ can be time dependent, subdivisions are necessary, whereby γ_0 is the experimentally observed, initial (frequently maximum) uptake coefficient and γ_{ss} is the experimentally observed, steady state uptake coefficient.
- b: The probability (per collision) that a gas phase molecule impinging on the solid surface resides on the surface for a finite time (non-elastic collision $>10^{-12}\text{s}$).
- c: The probability (per collision) that a gas phase molecule impinging reversibly on the liquid surface enters the liquid.

- d: The partition coefficient that describes the gas-surface partitioning at equilibrium. As described above, the Langmuir isotherm is most commonly used in various units. We report the partitioning coefficient in the limit of low coverage (linear dependence of coverage on gas concentration) where the units are as given above.
- e: The partition coefficient that describes the distribution of trace gas between the gas phase and condensed phase volumes. For a liquid particle this is the solubility, for a solid particle it will include the gas molecules that are associated both with the surface and with the volume of the particle.

Table 2: Methods used in the study of heterogeneous processes

A number of experimental techniques have been developed for the study of heterogeneous processes. Most methods rely on the determination of loss rates or time dependent concentration changes of gas-phase species in contact with a surface. These include low pressure coated surface laminar flow tube reactors and Knudsen cells for bulk surfaces and films, and droplet train reactors, aerosol flow tubes and static aerosol chambers for dispersed surfaces. Surface adsorbed reactants and products have frequently been observed using surface-sensitive techniques, such as reflectance infra-red spectroscopy (DRIFTS, RAIRS), and these have in a few cases been applied to kinetics studies. A list of the related abbreviations used in the data sheets is given below.

Methods	
CWFT	Coated Wall Flow Tube
CRFT	Coated Rod Flow Tube
AFT	Aerosol Flow Tube
Knudsen	Knudsen Reactor
DT	Droplet Train
LJ	Liquid Jet
BC	Bubble Column
PBFT	Packed Bed Flow Tube
Detection	
AMS	Aerosol mass spectrometry
ATR	Attenuated total reflectance spectroscopy

APS	Aerosol particle sizer
DRIFTS	Diffuse Reflectance Infra red Fourier Transform Spectroscopy
DMA	Differential mobility analyser
RF	Resonance Fluorescence
CL	Chemi-Luminescence
GC	Gas Chromatography
MS	Mass Spectrometry
MBMS	Molecular beam sampling MS
CIMS	Chemical Ionisation Mass Spectrometry
UV-Vis	Ultra-Violet absorption spectroscopy
SR	Static Reactor
SMPS	Scanning Mobility Particle Sizer
TIR	Transmission Infra red spectroscopy
TEM	Transmission Electron Microscopy
RC	Counting of decays of radioactive isotopes

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