We thank all three reviewers for their careful readings of our manuscript and useful suggestions on how to improve our presentation. All three reviews are reproduced below, with our responses interspersed (in red) after their comments and questions. Some key sections of revised text are also included, with new or revised portions highlighted in red.

Review of "An overview of current issues in the uptake of atmospheric trace gases by aerosols and clouds, by Kolb et al.

This manuscript describes the state-of-the-art in the field of atmospheric heterogeneous kinetics. The authors, from a variety of US, Canadian and European research groups bring together a wealth of expertise and experience to generate a (justifiably) lengthy text. Being too general for the knowledgeable practitioner in this field yet too detailed for those hoping for a quick insight it is not always clear for which audience this was written. The manuscript has a "white paper" feeling to it and whilst demonstrating that significant progress has been made over the last decade it also indicates where improvements in data quality are required and also possible areas of future research. The inconsistent levels of detail presented for different chemical systems / surfaces presumably reflects different authors and is probably unavoidable in a document of this type.

Response – We appreciate the reviewer's analysis and agree that this manuscript is fairly described as a "white paper" style review, designed to catalog progress in a rapidly developing research field, while also presenting areas where future research could produce improved data and understanding. In response to more specific suggestions below we have attempted to make the treatment of different chemical systems/surfaces more consistent.

One area where I feel that the authors have missed an opportunity is the lack of linkage to the recent IUPAC publication covering heterogeneous reactions on solid surfaces in the same journal. In many ways these two articles would both gain significantly in impact if close links were built in. The IUPAC document lacks the general overview, which Kolb et al provide, yet does give a high level of detail for individual trace gas – surface interactions that is not available here. As several of the authors are common to both papers, linking them can surely be accomplished without too much effort, most easily in section 5.2 but also in the introductory text.

Response – The following text has been added to Section 1.2 of the revised manuscript:

In recognition of these needs the topic of heterogeneous processes involving atmospheric trace gases has been included in the evaluations carried out by the NASA-JPL data evaluation panel. In their most recent full evaluation (Evaluation 15, July 2006; http://jpldataeval.jpl.nasa.gov/download.html) heterogeneous reactions in the stratosphere

and selected heterogeneous processes in the free troposphere are addressed. More recently the IUPAC Subcommittee for kinetics data evaluation for atmospheric chemistry have undertaken an evaluation of data for heterogeneous reactions which is presented on the IUPAC website at University of Cambridge, UK. (http://www.iupac-kinetic.ch.cam.ac.uk/). Publication of this comprehensive evaluation for uptake on solid surfaces in Atmospheric Chemistry and Physics is currently in the final stages (Crowley et al., 2010). A further publication of evaluated data for uptake on liquid surfaces will be submitted to ACPD in 2010.

In addition, the following text has been added after the first sentence in Section 5.2:

The solid surfaces considered for atmospheric studies, as listed in the introduction to the evaluation heterogeneous processes on the IUPAC website at University of Cambridge, UK. (http://www.iupac-kinetic.ch.cam.ac.uk/), are: ice (usually in polycrystalline form); NAT (nitric acid trihydrate), NAD (nitric acid dihydrate) and SAT (sulfuric acid tetrahydrate); Mineral oxides (as on naturally occurring dusts); soot (usually amorphous black carbon); and solid electrolyte salts below their efflorescence temperature. The IUPAC evaluation provides recommendations for uptake coefficients on these surfaces, except for soot and solid salts. A manuscript covering much of this material is close to final publication in Atmospheric Chemistry and Physics (Crowley et al., 2010).

Overall the paper of Kolb et al. is a valuable contribution to the field, and it should be published. The authors should consider revision in line with some of the comments below.

In section 2.2 terminology is discussed. Please indicate whether the recommendations are entirely consistent with the PRA or IUPAC usage and definitions, otherwise further confusion will result. In this context, define S, Cg, αm and $\beta(\alpha$m) in section 2.3

Response – The recommendations in Section 2.2.1 to 2.2.3 are based on the PRA framework, which integrates and generalizes earlier approaches and introduces a clear distinction between surface and bulk accommodation (Pöschl et al., 2007). The recommendations are also consistent with the terminology recently adopted by IUPAC (Crowley et al., 2010). This information will be added in section 2.2.

The parameters/symbols listed in Section 2.3 (S, Cg, α_m and $\beta(\alpha_m)$) were actually not meant to be recommendations. They were just meant to reflect some of the parameters/symbols frequently used in the different model approaches and cited references. To avoid confusion, we will remove the (incomplete and unnecessary) listing of parameters/symbols from Section 2.3 in the revised manuscript.

Section 3. This deals with the various methods used for study of heterogeneous processes, with four selected as the most "successful". I feel that if figures are warranted then so is a better and more detailed analysis of the range and limitation of each method. The droplet train, Knudsen reactor, coated wall tube and aerosol flow tube all have

certain drawbacks. For solid surfaces, I am aware of only few examples where quantitative data from a Knudsen reactor has found its way into a model, whereas coated wall tubes have contributed substantially to the study of heterogeneous processes on e.g. ice and H2SO4, and droplet train and aerosol flow tube to study of aqueous surfaces.

Response – The discussions of each experimental technique in Section 3 have been expanded, as suggested. The revised section 3 of the manuscript is reproduced below with the additions and revisions reproduced in red. The Knudsen cell reactor description has been retained (and expanded). Knudsen flow reactors have the advantage that all exposed surface elements of the substrate are in the same state of saturation /subsaturation at any given time and so present a real-time response to the exposure of the substrate by a trace gas. In addition, coated-wall flow tube studies rarely present experimental rate laws as most studies assume first order kinetics, which may not apply. In fact, true first order kinetics is the exception, not the rule! Knudsen reactors allow one to check the rate law using different apertures in a straightforward manner.

3. LABORATORY TECHNIQUES FOR MEASUREMENT OF TRACE GAS UPTAKE

A variety of techniques have been devised to meet the challenge of quantitative measurement of uptake kinetic parameters in multiphase systems. We present here only a brief description of four of the most successful methods that have been used in recent years for this purpose. Descriptions of these and additional techniques can be found in Danckwerts (1970), Kolb et al. (1995) and Davidovits et al. (2006).

3.1 Droplet Train Flow Reactor

The droplet train flow reactor (Figure 1) is a technique used to measure the rate of uptake of gases into liquid droplets for particle size ~ 50-200 µm. It was first developed by the Aerodyne Research/Boston College Group (Worsnop et al. 1989) for measurement of accommodation coefficients of reactive trace gases in aqueous substrates.
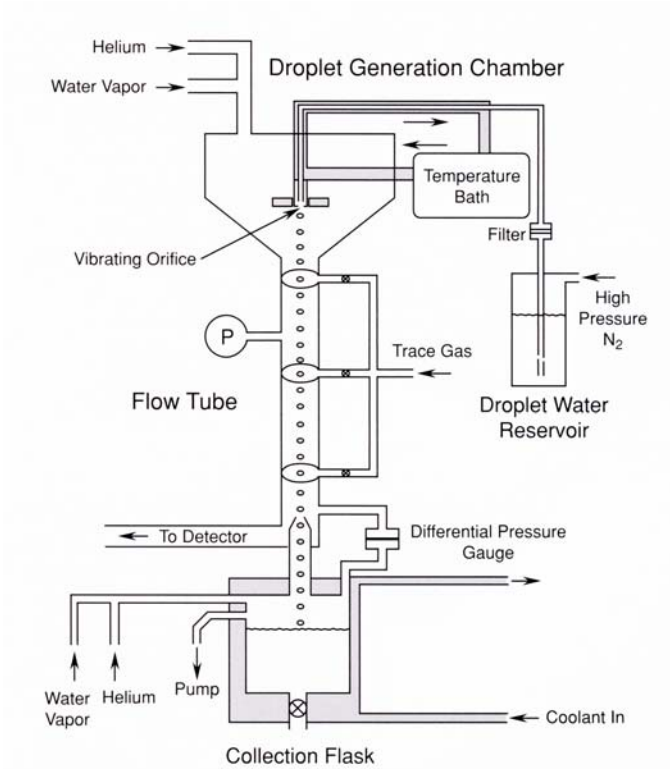
Figure 1. Schematic diagram of typical droplet train flow reactor for measurement of uptake coefficients of trace gases into liquids (adapted from Jayne *et al.*, 1992).

It is comprised of a droplet generation chamber, which ejects droplets of uniform size and spacing via a vibrating orifice into a flow tube at linear flow velocities typically in the range (1500-4500) cm s^{-1}, and total pressure in the range 6-20 Torr. The surface/volume ratio in the reaction zone is typically 10^{-3} cm^{-1}. Temperatures of the droplets lie in the range ~260-290 K determined by the H_2O vapor pressure in the tube. The reactant gas can enter the flow tube at various positions and changes in the concentration of the reactant gas, Δ_n, are measured at the downstream end following exposure to the droplets. Typical detection techniques used for trace gases are mass spectroscopy and tunable diode infrared laser spectroscopy. The droplets leaving the interaction zone can also be collected and analyzed, typically using liquid chromatography methods, to determine changes in composition resulting from uptake.

The measured uptake coefficient can be evaluated from the ratio of the number of gas molecules taken up per second, $(F\Delta_n)$, over the total number of gas droplet collisions, $\left(N^*AN_g\overline{c}\right)/4$:

$$\gamma = \frac{F\Delta_n}{\dfrac{N^*AN_g\overline{c}}{4}}$$

where F is the bath gas flow rate, N^* the number of droplets which react with the gas, A the droplet surface area, N_g the number of molecules of reactant gas per unit volume, and $\bar{c}$ the mean molecular speed. In practice it is convenient to measure the fractional change in gas concentration as a function of change in droplet surface area in contact with the trace gas. The surface area exposed to the trace gas is varied either by changing the applied frequency of the vibrating orifice or by a change in the droplet-gas interaction distance. The normal transit time in the reaction zone is ~1 – 30 ms, which is generally sufficient to avoid saturation of the surface. Very large uptake coefficients, requiring shorter contact times, can be achieved by injecting droplets transversely through holes in the side of a horizontal flow tube. If uptake coefficients are large, leading to significant concentration gradients, corrections may be required for gas phase diffusion. This requires knowledge of the diffusion coefficient of the trace gas in the appropriate carrier gas (usually He). Description of the mass transport in the gas phase is a key factor in obtaining accurate uptake rates using this technique.

An important aspect of the experimental technique is the careful control of all the conditions within the apparatus. All experimental parameters are computer monitored and controlled: pressure (typically 6 - 20 Torr); water partial pressure (1.7 - 16 Torr); temperature (260 – 290 K for pure water droplets); and gas interaction time (1 – 30 ms). The range of γ values which can be measured is 10^{-3} – 1.0, although the detection limit is extended to ~10^{-5} using liquid phase analysis. Experiments to date have been performed with water at various pH levels, aqueous salt solutions, organic liquids, and sulfuric acid from 20 – 70 wt% H_2SO_4 (at temperatures down to 230K).

3.2. Knudsen Cell

The use of a Knudsen Cell for surface uptake studies was pioneered by David Golden and co-workers at Stanford Research Institute (SRI, now SRI International) (Golden et al., 1973; Quinlan et al, 1990) A schematic diagram of a typical Knudsen cell is shown in Figure 2. Knudsen cells are operated at pressures <10 mTorr to ensure that the mean free path of the reactant gas exceeds the diameter of the exit orifice by at least a factor of three. In this way molecular flow conditions apply and gas phase diffusion effects are avoided. The reactant gas enters the cell at a known flow rate and exits it via an orifice of known size connected to a very low-pressure system. Detection is usually by modulated molecular beam mass spectrometry. As the reactant gas flows through the cell it is exposed to a sample surface, which may absorb, adsorb or react with the trace gas. Multiple orifices enable the measurement of the uptake rate as a function of pressure, which can be varied by up to a factor of two hundred. The first-order rate constant for the heterogeneous reaction, k_r, and the uptake coefficient, γ, can be evaluated from the difference in reactant gas concentration both in the presence, N_r, and absence, N_0, of the sample surface (which can be masked from the main cell volume) using the following equations:

$$k_r = k_{esc}\left(\frac{N_0 - N_r}{N_r}\right)$$

$$\gamma = \frac{A_h}{A_s}\left(\frac{N_0 - N_r}{N_r}\right)$$

Here k_{esc} is the effective first-order rate constant for escape of the gas from the cell through the exit orifice, which can be evaluated experimentally or from kinetic
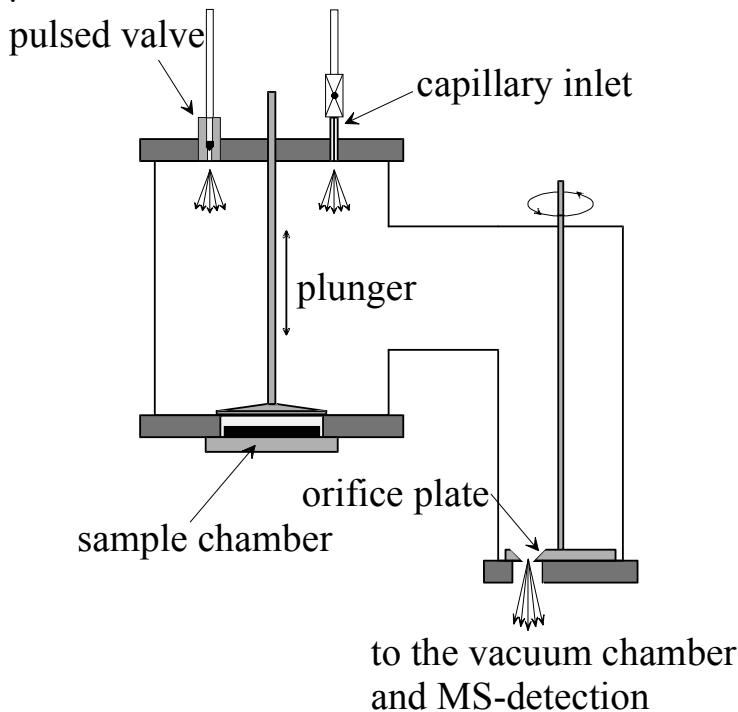
.

Figure 2. Schematic of a Knudsen cell for the investigation of heterogeneous reactions using either continuous flow or pulsed gas admission. The rotatable orifice plate can put up to four molecular-beam forming orifices into line of sight with the ionizer of the mass spectrometric (MS) detector (from Caloz et al., 1997).

molecular theory; A_h and A_s are the surface areas of the exit orifice and of the sample respectively. Typical surface/volume ratios are 4×10^{-4} to 8×10^{-2} and by varying the relative size of A_h and A_s a range of γ between 1 and 10^{-5} can be measured accurately. This range of γ has been extended to 10^{-6} and below when the sealed-off sample compartment is used as a static reactor for the trapped gas phase at reaction times of minutes (Caloz et al., 1997).

The timescale for conducting uptake measurements in a Knudsen reactor is many seconds and hence surface saturation is often difficult to avoid and consideration must be given to the possibility of re-evaporation into the gas phase following uptake, giving time

dependent uptake. Similarly, accumulation of products on the surface may change their reactivity. These effects lead to time dependent γ which can offer useful information if measurements can resolve the changes adequately. Both pulsed gas admission as well as continuous flow of gases, have been used to investigate such behavior.

The main advantage of the Knudsen reactor is the avoidance of diffusion effects when uptake is very efficient. However the need for very low operating pressures means that surfaces with high vapor pressures cannot be studied. This is a major limitation for atmospheric processes as it precludes studies on liquid water and ice at temperatures above ~215 K, although uptake on sulfuric acid at stratospheric temperatures can be studied. Uptake on solid substrates can be measured over a wide temperature range.

3.3. Flow Tube Reactors

3.3.1 Coated wall flow tube reactor

Coated and wetted wall flow tubes have been used extensively to measure uptake and reactions of gases with both liquid and solid surfaces. Figure 3 shows a schematic diagram of a typical flow tube system used in the investigation of the uptake of trace gases onto ice. The wall of the 1.5 cm diameter x ~50 cm length flow tube is coated
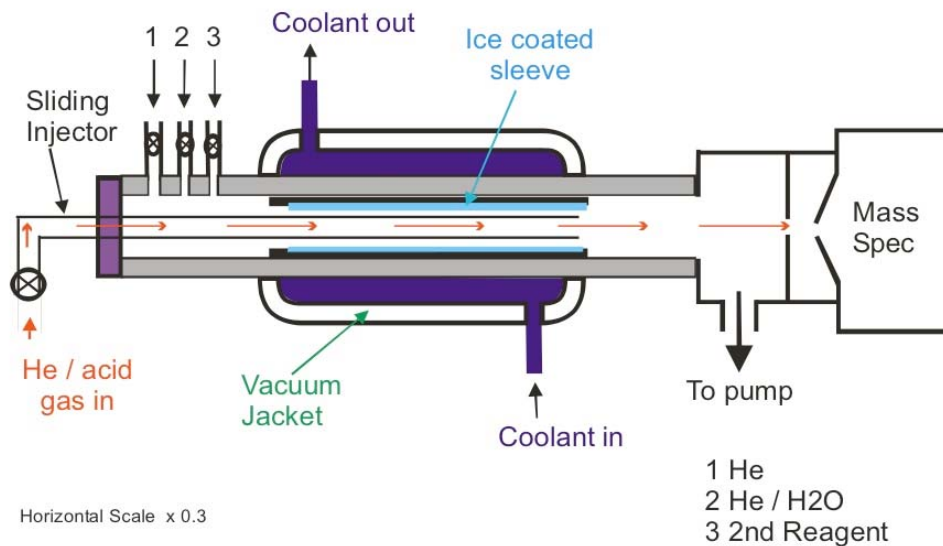

Figure 3. Schematic of flow tube used for measurements of uptake of trace gases on ice (Symington, A.M., 2009). A smooth ice film is produced by freezing pure water on the inside of a liner inserted into the flow tube held at 258 K. The trace gas diluted in He is introduced via a sliding injector.

with the condensed phase of interest (e.g. ice, salt/mineral dust layer or liquid film). The carrier gas (usually He, N_2 or Ar) travels under laminar plug flow at $500 – 3000$ cm s^{-1} along the tube and enters the detector system downstream of the surface. The tube is jacketed allowing circulation of thermo-stated fluid to control temperature (range typically $190 – 350$ K. Coated wall flow tube studies are generally carried out at low pressures (0.5-3 Torr) because of limitation in the diffusion rate of the reactant gas to the flow tube walls. For aqueous systems H_2O is usually added to the carrier to prevent evaporative loss from the wall coating.

The reactant gas is added through a sliding injector. By varying the distance between the sliding injector and the detector, the time of exposure of the reactant gas to the condensed phase can be varied, allowing a pseudo-first order rate constant for removal of the gas, k_s, to be measured, provided there is not significant surface saturation. Alternately the total amount of trace gas adsorbed on a prescribed surface area can be measured over a period of time at a fixed distance, providing information on surface coverage at saturation. This can be used to investigate adsorption characteristics and determine partitioning coefficients, e.g. to ice surfaces.

A variety of on-line sensitive detection schemes have been used, generally either spectroscopic or mass spectrometry with differential pumping (MS). Electron impact MS has been widely used. Additional sensitivity and selectivity has resulted from recent developments in chemical ionization mass spectrometry (CIMS). Optical detection techniques have included laser-induced fluorescence, UV and IR absorption and chemi-luminescence.

The net uptake probability from coated wall flow tube experiments can be evaluated from:

$$\gamma = \frac{2rk_s}{\overline{c}}$$

where r is the radius of the tube and $\overline{c}$ is the mean molecular speed. Correction of observed uptake rates for diffusion limitation can be made using the correction procedure described by Brown(1978), which can be applied if gas phase diffusion coefficients are known. Limits imposed by gas phase diffusion determines the upper limit for accurate uptake coefficient measurement of ~0.2 in wall coated flow tubes. Uptake coefficients down to 10^{-5} can be measured, making this a very versatile method for uptake measurements.

In the case of liquid surfaces a vertically mounted wetted wall flow tube is the favored configuration. The inside wall of the tube is completely covered with a slowly flowing film of the liquid of interest, which enters the tube via a lip or grooved joint to produce an even film. Thus the liquid surface is constantly renewed so that a surface of constant composition, free of saturation and reaction products, is obtained. An important limitation for aqueous liquids is the requirement for modest water vapor pressures to maintain a defined gas diffusion regime. Thus temperatures are restricted to $260 – 293$ K. A second

In a recent paper Davis (2008) has published a detailed analysis of the interpretation of flow tube data for gas uptake measurements and reviewed the literature on flow tubes. The new analysis consolidates data obtained in earlier work for various flow rates and trace gas concentrations.

3.3.2 Aerosol flow tube reactor

This type of system was first used for uptake coefficient measurements of ammonia on sulfuric acid droplets by Robbins and Cadle (1953), Huntzicker et al. (1980) and McMurray et al. (1983), and the free radical, HO_2, by Mozurkewitz et al. (1987); it has subsequently been improved and developed by several groups, making use of novel technology in aerosol generation and characterization.
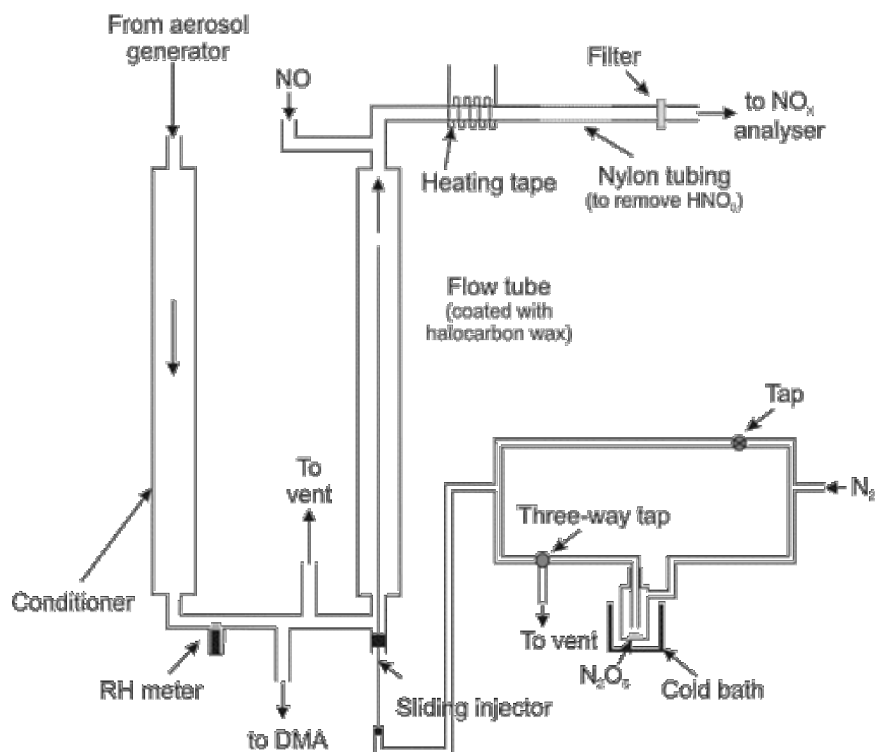

Figure 4. Schematic of aerosol flow tube for measurements of uptake coefficients (from Badger *et al.*, 2006). In this case N_2O_5 was measured using a chemiluminescence method after titration with NO added at the reactor exit.

Figure 4 shows a schematic diagram for an aerosol flow system used to determine the uptake coefficient of N_2O_5 on aqueous aerosols. Submicron aerosols are generated in a nebuliser containing an aqueous solution or suspension of the desired substrate. The suspended particles are diluted in carrier gas (usually N_2 or air), dried in a diffusion-dryer, re-humidified to the desired relative humidity, and passed through a conditioner where the aerosol equilibrates to the temperature and humidity conditions. The aerosol flow is split and one stream is directed to a differential mobility analyzer where the size distribution of the conditioned aerosol is determined. Charged particles need to be neutralized to avoid rapid loss if inlet lines and flow tube walls are not conductive. Another stream enters the flow tube at the upstream end and the excess flow is vented. The total pressure is normally 1 bar and the flow speed $\sim$ 1-3 cm s^{-1}, but the system can be operated at 100 mbar or less.

The reagent trace gas is diluted in carrier gas and enters the reactor through a sliding injector, allowing different exposure times to the aerosol, before detection at the reactor outlet. Attention needs to be given to the flow conditions required for establishment of laminar flow and mixing from the injector. This restricts measurements to the central portion of the flow tube but kinetic decays can normally be achieved over a useful time domain, and loss rate coefficients determined. Measurements for k_s have to be corrected for wall losses, hence uptake coefficients are determined by measuring the rate of loss of the reactant gas in the presence and absence of aerosol, with suitable corrections for concentration gradients produced by wall losses (Brown, 1978). The following equation is used to evaluate γ:

$$\gamma = \frac{4k_s}{\bar{c}S_a}$$

where S_a is the aerosol surface area per unit volume carrier gas. This is determined from the measured size distribution, which for soluble salt aerosols generated in a nebuliser, typically has a geometric standard deviation of $\sigma = 1.5 - 2$ and a mean area weighted radius of $\sim$120 nm. A calibrated scanning mobility particle sizer provides the integrated S_a, which can be varied over the range $10^{-5} - 10^{-3}$ cm^2/cm^3. S_a corresponds to the surface area of spherical particles with the same electrical mobility as those of interest. Therefore, a careful analysis is required to evaluate the true surface area for non-spherical particles. While the systematic error in S_a determined this way may be significant, e.g., 30% for mineral dust aerosol (Vlasenko et al., 2006), it is still much less than the large uncertainty associated with the evaluation of experiments using bulk powder substrates. This method has been used for accurate measurements of uptake coefficients of between 1.0 and 10^{-4} and on a range of inorganic and organic liquid particles and also on solid electrolytes and dusts. Careful control of all the conditions within the apparatus is achieved by using flow sensors and input flow valves operated under computer control.

Detection of trace gas concentration changes at the ppb level at 1 bar required for the AFT method has been mainly achieved via CIMS, which has potential for sensitive and

selective measurement of a variety of species. Chemiluminescence analysis has been employed, e.g. for NOx species and for HO$_2$. Alternately, the aerosol can be collected and the uptake determined by analysis of changes in the composition of the condensed phase.

3.4. Cloud Chamber

Cloud chambers are commonly used for investigations of droplet formation and growth under well-defined thermo-physical conditions. After vapour super-saturation has been established inside the measurement chamber, aerosol particles initiate formation of droplets, which subsequently grow by condensation. A schematic diagram of the expansion cloud chamber can be seen in Figure 5. Vapor super-saturation is achieved by adiabatic expansion from the expansion chamber (EXP) allowing rapid establishment of well-defined and uniform conditions inside the measurement chamber, which has been previously charged with a well characterized mono-disperse aerosol (~1.2 x 10^4 particles cm^{-3}) from an electrostatic classifier and a humidifier unit (H). The pressure prior to expansion is measured on a gauge (PG) and the system allowed attaining thermal equilibrium with partial pressures in the expansion chamber slightly below the humidifier. Expansion is achieved by opening the valve (V2) between the expansion chamber and the much larger low-pressure buffer tank (R), leading to practically zero change in total pressure after the expansion.

Droplet growth is quantified using the constant angle Mie scattering (CAMS) method (Wagner, 1985), providing absolute, time-resolved, and non-invasive simultaneous determination of droplet diameter and number density. Mass and thermal accommodation coefficients can be determined from quantitative comparison of experimental and theoretical droplet growth curves. For the sizes and growth rates of the droplets considered a clear and accurate theoretical description is obtained using state-of-the-art condensation models (Vesala et al., 1997). Mass and heat fluxes to/from the droplets are calculated accounting for depletion of vapour as well as the production of latent heat in a population of growing droplets. As droplet growth is at least partly under gas kinetic control, both mass and heat flux need to be corrected by the corresponding transition regime correction factors (Fuchs and Sutugin, 1970)

$$\beta_m = \frac{1 + Kn}{1 + \left(\dfrac{4}{3\alpha_m} + 0.377\right)Kn + \dfrac{4}{3\alpha_m}Kn^2}$$

and

$$\beta_t = \frac{1 + Kn_t}{1 + \left(\dfrac{4}{3\alpha_t} + 0.377\right)Kn_t + \dfrac{4}{3\alpha_t}Kn_t{}^2},$$

respectively. Here, Kn and Kn_t represent Knudsen numbers for vapour and carrier gas molecules given by the ratio of the corresponding mean effective free path and the droplet radius, and α_m and α_t denote mass and thermal accommodation coefficients. Variation of the total gas pressure inside the expansion chamber allows independent determination of α_m and α_t, respectively (Winkler *et al.*, 2004, 2006).
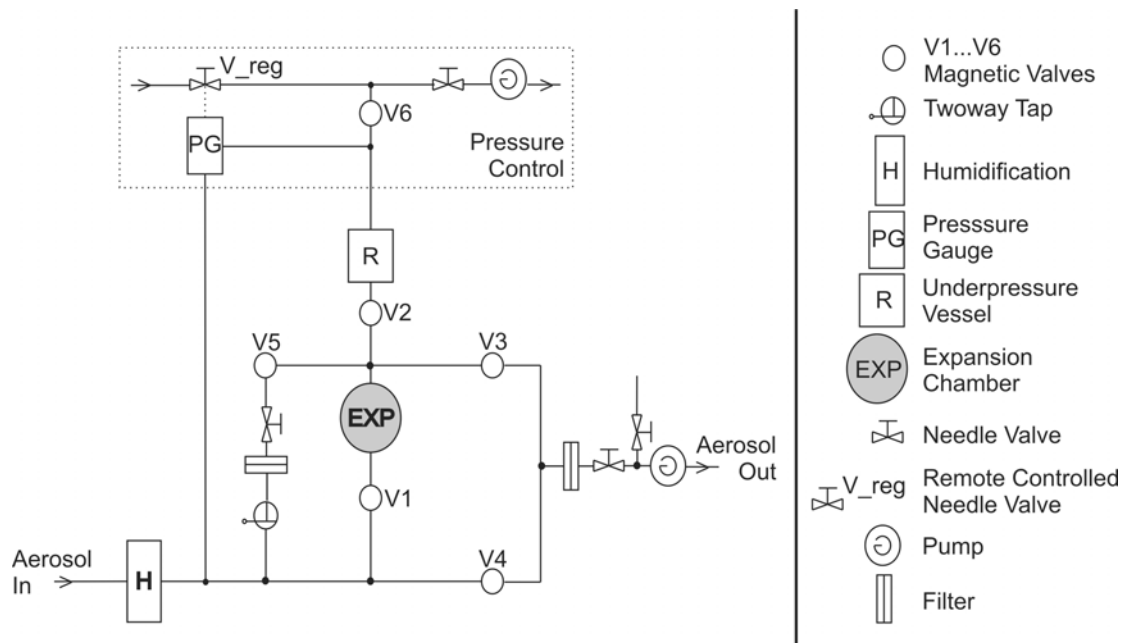

Figure 3.5. Schematic diagram of the expansion cloud chamber showing the main components for pressure and flow control.

P11159: In the equation on top of page: c should be $\bar{c}$.

Response – The suggested change has been made in that equation and several others, as well as the text. See revised Section 3 text above.

P11159, L11: "An alternative approach" is a bad way to start a new section (alternative to what ?)

Response – See revised text at the start of sub-section 3.3.2 above.

P11180, L8: "on the face of it" is too colloquial

Response – The offending language has been changed to "There is fairly good agreement

among the measurements: all suggest….”

P11184, L14: I’m not sure why IUPAC is cited here ?

Response – Reference to IUPAC will be removed

P11186, L5: An atmospheric trace gas is not (neither strictly nor remotely) a surfactant film, Please re-phrase.

Response - The offending language has been changed to ”While difficult to relate to atmospheric conditions, surfactant films have been shown to…..”

P11188, L18: Solubilities of HCl and HNO3 are low in ice.......please provide reference(s).

Response - Among the many possible references two representative ones will be cited, one for HCl and one for HNO_3 solubility, respectively: (a) HCl/H_2O Solid-Phase Vapor Pressures and HCl Solubility in Ice, D.R. Hanson and K. Mauersberger, J. Phys. Chem., 94, 4700-4705, 1990; (b) E. Thibert and F. Dominé, J. Phys. Chem. B, 102, 4432-4439, 1998.

P11191, L1: Have experiments at atmospherically relevant HNO3 concentrations observed a decrease in the ice evaporation rate?

Response - This is an excellent question that deserves a thoughtful response. So far there are only laboratory experiments in which H_2O evaporation rates of ice as a function of dose of adsorbed HNO_3 (not HNO_3 concentration!) have been measured. However, a back-of-the-envelope (really!) calculation of the time required to deposit10% of a monolayer of HNO_3 on dense cirrus (10^{-4} S/V) results in 12.8 hours. The conditions were: T = 210 K, γ = 0.1, $[HNO_3]$ = $2x10^{10}$ molecules cm^{-3} at 20 km altitude. It is easier to manipulate dose than partial pressure of HNO_3 in laboratory experiments. However, the answer is of atmospheric relevance, with the exposure parameters all scaling linearly. For instance, the time is halved for γ = 0.2 (for 200 K), and for each decrease of the S/V ratio there is an increase by an order of magnitude of the time required to deposit 10% of a monolayer.

P11191, L20-25: There are several theoretical studies of the bonding of trace gases to ice surfaces which reveal interesting aspects of the interaction and also provide adsorption enthalpies with which to compare experimental data. Perhaps some of these deserve mention.

Response – We agree that there are interesting results coming from the theory (periodic DFT calculations), see for instance Jedlovsky et al., J. Amer. Chem. Soc., 128, 15300-15309, 2006, and others. However, we do not believe that these theoretical studies are of immediate atmospheric relevance, although they may be helpful at understanding and interpreting laboratory results. Until the gas-atmosphere interface is modeled more realistically we may have to postpone any assessment as to the degree of realism of such calculations. It is by no means certain that the atmospheric ice interface corresponds to a flat single crystal ice surface in the presence of trace gases. The same also goes for DFT calculations of adsorbed species on mineral dust substrates: nice to have, but of questionable value regarding atmospheric relevance (see for instance Baltrusaitis et al., Phys. Chem. Chem. Phys., 9, 4970-4980, 2007).

P11192, L10: _ has a small but significant..............what trace gas is the text referring to

Response - H_2O vapour, the text of the revised manuscript will so indicate.

P11194, L9: How are nitrates and sulphates formed from non-reactive uptake onto mineral dust ?

Response - "Non-reactive" refers to bulk non-reactivity, in contrast to $CaCO_3$ that shows bulk reactivity towards acidic gases. Surface vs. bulk reactivity will specifically be emphasized in the revised version of the manuscript.

P11194, N2O5 and SO2 uptake to mineral dust. How does the uptake coefficient depend on relative humidity ? This should be mentioned.

Response - There are quite a few laboratory results that report the dependence of the uptake kinetics of trace gases on relative humidity (RH), although the dependence is often weak or sometimes absent (see Baltrusaitis et al., Phys Chem. Chem. Phys., 9, 5542-5554, 2007). However, there are exceptions (Liu et al., J. Phys. Chem. A, 112, 1561-1571, 2008; Vlasenko et al., 2006; Mashburn et al., J. Geophys. Res., 111, D15213, 2006), thus every case needs to be investigated. In a number of cases one observes a small increase of γ at low RH, a peak g value at 30-60% RH (depending on the trace gas under study), and a gradual decline of g at high values of RH. The effect of water vapour is likely related to the solubility of the trace gas under question, its influence may be through competition for surface adsorption sites or due to promoting solvation at the surface. Therefore it may lead to both positive and negative dependence of γ on relative humidity or also a combination thereof over the full humidity range. Appropriate text and reference(s) will be added in the revised manuscript.

P111196, L17: A similar example.........differ by three orders of magnitude. Which

approach provides the larger value of γ?

Response - Measurement of gas-uptake (γ measured from the decay/consumption of reactant gas) provides the larger values of γ compared to DRIFTS measurements (γ measured from the accumulation of reaction products on the substrate surface). However, the discrepancy has narrowed recently, but significant differences remain (see Mashburn et al., J. Geophys. Res., 111, D15213, 2006). Part of the discrepancy may also be attributable to difficulties with the calibration of IR bands using chromatographic methods after leaching the adsorbed species (anions) from the substrate. The point is that the geometric surface area is the correct surface metric to use as opposed to the BET surface area in evaluating initial values of γ from gas uptake. Results using gas uptake on aerosols studied in aerosol (slow) flow tubes under steady-state conditions point to the validity of a total external surface metric commensurate with the equivalent aerosol diameter (Wagner et al., 2008). Clarifying text will be added to the revised manuscript.

P11196, L22: ..."the insoluble/soluble transition should be taken into account". Not sure what this is trying to say.

Response - This sentence will be deleted.

P11196-111197. There is (too) much discussion of BET versus geometric surfaces. In a nutshell, experiments using bulk porous samples, whether Knudsen or coated wall flow tube are problematic. The aerosol flow tube solves some but not all the problems. How does e.g. the AFT experiment cope with non-spherical particles ?

Response - We strongly agree with the referee that each experimental method has advantages as well as disadvantages. However, there are disparate γ values for identical and/or similar substrates in the published literature that need an explanation or a comment. One of the problems is that one almost forgets to mention the primary measured parameter of interest, i.e. the rate constant for heterogeneous reaction (k_{het}). In cases where there is a three to four orders of magnitude discrepancy between γ's for essentially the same k_{het} (surface-to-volume ratios do not change that much from one reactor to the next) one needs to be reminded which is the surface metric, geometric, total external or BET. The maximum difference amounts to typically three to four orders of magnitude in γ values. In comparison, the non-spherical nature of some particles leads to a significantly smaller uncertainty, on the order of less than an order of magnitude in γ.

P11198, L18: The role of co-adsorption of traces gases is largely unexplored....... Co-adsorption might not be the main issue. Mineral dust can be rapidly chemically aged in polluted air masses. The role of aging (and loss of reactivity) due to exposure to especially, O3, HNO3 and SO2 are important questions as is the rate of re-activation by

H2O. The rate of bulk dissolution of basic components of mineral dust is also of great importance (Sullivan et al, Phys. Chem. Chem. Phys, 2009).

Response - Agreed, aging of mineral dust by oxidants and changes in surface composition and reactivity are important issues, although mineral oxides that are important constituents of mineral dust are already at the highest possible oxidation state of a particular substrate. We therefore expect minor changes of surface properties upon chemical aging of mineral dust aerosol. What is meant by coadsorption is the reactivity change of the gas-solid interface at high values of RH as both the oxidant and H_2O vapor are competing for the same surface sites (see above). A clarification will be added to the revised text. We can cite the Vlasenko et al. (2009) paper highlighting the decreasing reactivity of dust with continued exposure to HNO_3, due to surface deactivation on dust not only containing CaCO3 and the fact that dissolution of basic cations out of silicate minerals is generally slow. We will also cite the already referenced Sullivan et al. paper in order to close the book on the unsurprising and umpteenth publication on the aerosol $CaCO_3$ component's reactivity in the presence of HNO_3.

P11199, L20-21. How about H2O2 ? There is a recent study in ACPD (Pradhan et al, 2010).

Response - Although interesting and of high quality, this paper is scheduled to be published shortly in ACP. The cut-off date for this review is approximately March 2010, which is the reason that it has not found its way into the review. We will, however, review the paper again if it is published before we have to submit the final version of our manuscript and reconsider including it at that time.

P11200, L11: characterised should replace governed.

Response - Agreed.

P11200, L30: Do not start the sentence with "it" (what affects soot reactivity ?)

Response - Agreed, aging affects soot reactivity.

P11201, L15: define PAH

Response – Will do so.

P11201, L17-18: ...it appears that the RATE OF trace gas uptake ....faster than the RATE of reaction of the adsorbed PAH.

Response – Agreed – will revise.

Figure 3. Poor quality labelling. Why acid gas and not trace gas ?

Response – Changed (see revised Section 3 text above.)

Figure 4. Poor quality labelling. Appears to be specific for N2O5 uptake rather than a general experimental design

Response - Clarifying sentence added to figure caption (see revised Section 3 text above.)

Figure 5. Diagram does not really help to understand the principal of operation.

Response – Operational details have been added to the text of this subsection (see revised Section 3 text above.)

Anonymous Referee #2
Received and published: 6 June 2010
This over view manuscript by Kolb et al., is an important service to the community that studies interactions of gases with atmospheric liquid and solid particles. A great deal of information has been processed in a systematic way that will be very useful, particularly to people star ting research in these areas. A gas molecule colliding with a surface can undergo multiple interactions, such as for example adsorption, surface absorption or uptake into the bulk phase. Although these processes have been studied for several decades, an accepted uniform nomenclature describing the various processes has so far not emerged. Further, often the same symbol is used to represent different processes and at times even the processes get confused. For example, some researchers have confused surface adsorption with mass accommodation. A ver y important and immediately useful par t of the manuscript is the chapter devoted to laying out the full scope of possible gas liquid interactions and presenting suggestions for unambiguous nomenclature. In this field, most experiments measure gas uptake in one form or another. However, experimental measurements seldom provide directly values for the basic physical parameters such as α_b (mass accommodation coefficient). The actual measurement contains that information but is also affected by experimental conditions such as diffusion of the trace gas of interest to the liquid or solid surface, the density of the trace gas, the shape of the surface and the gas-liquid interaction time, etc. The measured uptake coefficient has to be de-convoluted to provide the unambiguous basic parameter independent on experimental conditions. Kolb et al. present clearly and discuss the complexities of gas surface studies and review ways that these complexities can be treated. The article treats with particular care and at length interaction studies of gas phase species with water and aqueous surfaces in general. This is an appropriate choice because of the atmospheric importance of such interactions. The results of several experimental studies as well as computer simulations disagree

with each other. The authors do not take sides with any set of results or experimental and computational techniques. Rather, they discuss the complexity of interactions and measurements and in most cases they discuss possible sources of error. I agree with this approach. The manuscript presents all the relevant references and an interested reader can decide what reliability to attach to a given result. (The article contains nearly 400 references.) This approach is applied also to the second section of the manuscript dealing with interaction of gases with surfaces of ice, minerals, organic compounds and soot where likewise many conflicting results are encountered. In connection with gas-mineral interactions, the authors provide a section discussing "Outstanding issues and future work". I think such a discussion is very useful and will help to formulate future studies. In a few cases (for example the effect of films on N2O5 uptake) the authors speculate about the mechanism responsible for the observed results. I find this an interesting and useful change of pace from the rhythm of the usual review article. The final Section 6 oriented toward suggested future work, includes a summary of funding available for gas uptake research. In summary, this is a very important contribution that merits publication. I present a few suggestions that the authors might want to consider.

Response - Thank you for your supportive remarks. Note, that in response to your comments and those made by the following reviewer, we have more clearly identified, and, in some cases, enhanced, material on "Outstanding issues and future work."
Suggestions:

1. The uptake processes with their suggested coefficient designations
are presented in Section 2.2. It would be helpful if a simple schematic diagram illustrating the processes and coefficients were introduced to accompany this section.

Response – We agree with your observation and suggestion and will add the following text and figure at the end of section 2.1 (after line 14, p. 11144):

Figure 1 provides a simple schematic illustration of key processes and flux terms used to describe atmospheric gas uptake by atmospheric particles: gas kinetic flux of surface collisions (J_{coll}), the adsorption onto the particle surface (J_{ads}), absorption into the particle bulk (J_{abs}), desorption from the surface (J_{des}), and net uptake by the condensed phase (J_{net}). The red arrows indicate production and loss of chemical species by reactions at the particle surface (P_s, L_s) or in the particle bulk (P_b, L_b). Note that further refinements in the representation of the gas-particle interface region are needed to resolve interactions of multiple chemical species and reactive processes, especially at the surface of solid or highly viscous liquid particles (e.g.: distinction of sorption and quasi-static surface molecular layers for the description of Langmuir-Hinshelwood- or Eley-Rideal-type reacti ons (Pöschl et al., 2007; Ammann and Pöschl, 2007).
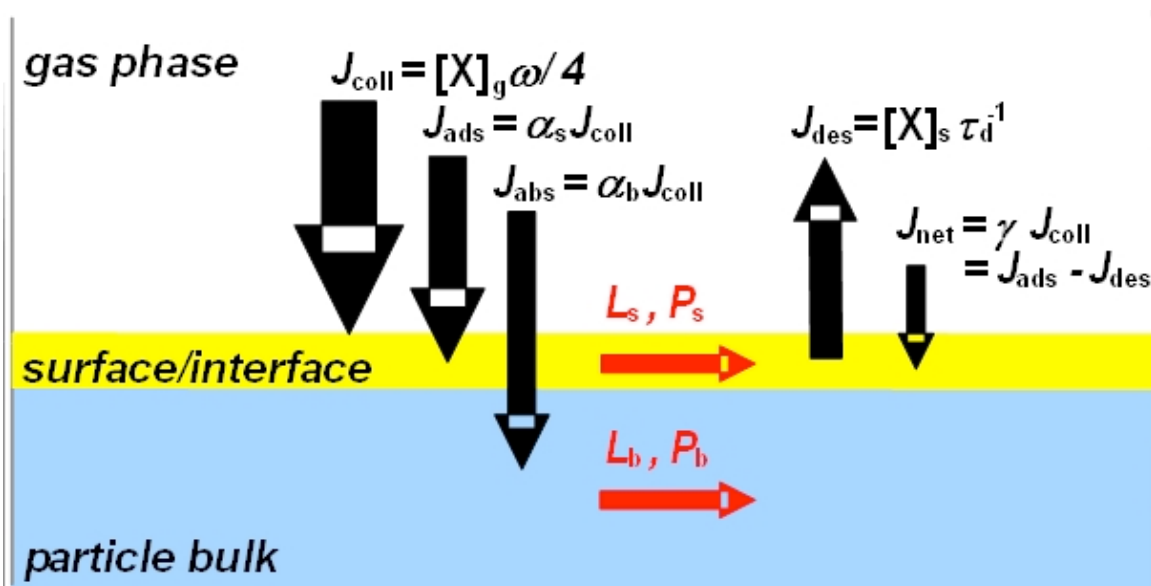
Fig. 1: Schematic illustration of key processes and flux terms describing gas uptake by atmospheric particles: gas kinetic flux of surface collisions (J_{coll}), the adsorption onto the particle surface (J_{ads}), absorption into the particle bulk (J_{abs}), desorption from the surface (J_{des}), and net uptake by the condensed phase (J_{net}). The red arrows indicate production and loss of chemical species by reactions at the particle surface (P_s, L_s) or in the particle bulk (P_b, L_b). $[X]_g$ and $[X]_s$ stand for the gas and surface concentrations of volatile species X; α_s and α_b are the surface and bulk accommodation coefficients; τ_d is the desorption lifetime, and γ is the net uptake coefficient.

2. It is noted in Section 2.2 that the coefficients Γ can have values greater than unity. This could be confusing. It might be helpful to add a paragraph something like: "Gas uptake into a liquid is generally described by differential equations that couple the various processes affecting uptake. Important simplifications result if these processes are decoupled. In many cases this is possible without significant loss of accuracy. The Γ factors are obtained by decoupling some of the specific processes. These factors are most often employed in the resistive gas uptake model where 1/Γ is the effective resistance due to the related factor limiting the uptake. These equivalent resistors are always in series with other effective resistors for example 1/αb. If Γ is large say, greater than 1, that simply means that the resistance to uptake due to that process is negligible compared to the bulk uptake coefficient."

Response – To avoid confusion, we intend to remove the capital Gamma terms from section 2.2.4. They are not needed to explain the basic features and differences of thermal accommodation, surface accommodation, bulk accommodation and net gas uptake, which are the subject of Sect. 2.2.

3. This survey article is written in the context of atmospheric chemistry. It would be helpful to discuss briefly how to determine which coefficients and under what circumstances dominate atmospheric gas uptake. Section 2.3.1 alludes to this issue by referring the reader to other articles. However, in this case I think two or three

paragraphs discussing specifics would be helpful.

Response – For clarification, we intend to re-number section 2.3.1 as section 2.4 (and 2.4 as 2.5) and to add the following paragraph at the end of section 2.3.1 (then 2.4):

Some studies have explored and compared the applicability and consistency of different modeling approaches (e.g., Shiraiwa et al., 2009, 2010; Pfrang et al., 2010; and references therein). A general consensus on the approach and level of detail required or best suited for different types of applications, however, has not yet been reached. Thus, researchers should evaluate on a case-by-case basis, which model approach is best suited for their application. When surface saturation effects are negligible and the rates of surface reaction and desorption are much lower than the rate of surface-bulk transfer, then bulk and surface accommodation coefficients are near-identical and independent of gas phase composition. Under such conditions, it will normally not be necessary to resolve surface processes. For bulk condensation or evaporation and absorption of gases by liquid aerosol and cloud particles, it should normally be sufficient to determine and use a bulk accommodation coefficient (traditional "mass accommodation coefficient") to characterize the molecular kinetics of gas-to particle mass transfer. To describe non-linear effects of surface reaction or surface saturation in Langmuir-Hinshelwood-type reactions on solid or highly viscous liquid particles, however, it will be necessary to distinguish surface and bulk accommodation and to resolve molecular kinetics at the gas particle interface (sorption layer vs. quasi-static surface layer, etc.). In studies investigating individual species and processes under steady-state conditions, the traditional resistor model approach may be suitable. Under transient conditions and for multiple -component/multi-process systems, however, it may be necessary to consider the full set of coupled differential equations describing mass transport and chemical reactions (Pöschl et al., 2007; and references therein).

4. The treatment of surface thermodynamics is out of keeping with the rest of the manuscript. No other topic receives the type of detailed mathematical coverage as is presented in this section. For example, the resistor model of uptake is described only a qualitatively (as I think is appropriate). I suggest that surface thermodynamics be likewise described only qualitatively and only as it pertains to gas uptake especially since this thermodynamic formalism seems to have no bearing on the rest of the text. If the authors decide to keep the section as is, they should point out that Γ in this section is not the same as the coefficient Γ presented in connection with gas uptake in section 2.2.2.

Response – Although we believe that this subject is not adequately covered elsewhere, we agree with the reviewer that this section is significantly different in style from the rest of the paper. Accordingly, we have removed the detailed mathematical coverage while keeping the overall sense of the section more in line with the surrounding sections. The new text for this Section 2.4 (to be renumbered in the revised version) is copied below.

2.4 Thermodynamics of Gas/Liquid Interfaces and Trace Gas Uptake

As noted above, interacting kinetic, thermodynamic and mass/heat transfer processes are involved in trace gas heterogeneous uptake. For instance, mass and heat transport occur simultaneously in condensation and evaporation processes due to the latent heat of phase transitions. Thus, simultaneous modeling of both mass and heat transport is often required for correct interpretation of experimental data, e.g. in experiments involving gas-to-particle conversion or high fluxes of gas accommodation to or evaporation from bulk liquid interfaces. Understanding the interplay of multiple physical and chemical processes is always challenging; however, convoluted interfacial processes pose a special challenge. Physicists and physical chemists have a long and successful history of characterizing thermodynamic, kinetic and heat/mass transfer processes in single phases and can draw on well established theories and models to describe and analyze their interplay in single phase systems. However, interfacial properties and processes are generally much less well characterized, often lacking even critical thermodynamic data.

2.4.1 The gas/liquid interface

At an air-aqueous interface, of a water droplet, for example, the strong hydrogen bonds associated with water give rise to a very high surface energy at the interface. The high surface energy may be reduced if surface-active species are present at the interface; this occurs spontaneously if the decrease in surface energy is sufficient to overcome the loss of full solvation by the surfactant species. Amphiphilic compounds, such as long-chain carboxylic acids and phospholipids, are good examples of this effect, since the hydrophilic head groups may be well solvated by surface water molecules, whereas the hydrophobic tails are not and are preferentially directed into the gas phase. However, even quite soluble compounds, such as dimethysulphoxide (DMSO) or ethanol, can be surface active (Donaldson, 1999; Mmereki et al., 2000; Donaldson and Vaida, 2006); that is, they may spontaneously partition to the air-water boundary in a proportion greater than that present in the bulk aqueous phase. Recently, some soluble inorganic anions (especially the larger halides) have also been shown to be surface active (Hu et al., 1995; Donaldson, 1999; Ghosal et al., 2005; Jungwirth and Tobias, 2006; Petersen and Saykally, 2006). The presence of compounds other than water at the interface clearly may affect both the surface properties and the chemistry there.

Insoluble, non-volatile surfactants, such as fatty acids, alcohols and other such species, have been identified in aerosols of marine origin. [Tervahattu, H; Hartonen, K; Kerminen, VM; Kupiainen, K; Aarnio, P; Koskentalo, T; Tuck, AF; Vaida, V, "New evidence of an organic layer on marine aerosols:, (2002) J. Geophys. Res. 107, #4053; Russell, LM; Hawkins, LN; Frossard, AA; Quinn, PK; Bates, TS, "Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting", (2010) Proc. Nat. Acad. Sci. 107, 6652-6657]. Such insoluble compounds exist exclusively at the interface and their film properties are generally expressed in terms of a film equation of state, such as a 2-D van der Waals analog. [Donaldson DJ and Vaida V, (2002) "The influence of organic films at the air-aqueous boundary on atmospheric

processes" Chem. Rev. 102, 1145-1461]. Such films may exist in 2-D analogs of gaseous, liquid and solid states, as the film becomes successively more compressed. By contrast, in studies of soluble surfactants, it is generally the surface excess, rather than the surface concentration, of adsorbate that is measured. This is defined as the amount of solute adsorbed to the surface relative to the amount of solvent, water in this case. The surface excess is given by the Gibbs equation, [Adamson, A. W.; Gast, A. P. (1997) "Physical chemistry of surfaces" J. Wiley and Sons, NY] which may be related to the adsorbed amount using an adsorption isotherm. For soluble surfactants, the concentration (or activity) dependence of the surface excess, at solute concentrations below phase separation, has generally been described by a Langmuir adsorption isotherm. This type of adsorption behavior implies that a finite number of independent adsorption sites exist at the aqueous surface, with a single enthalpy of adsorption, independent of surface coverage.

Analysis of adsorption isotherms obtained from the Gibbs equation (or from calibrated spectroscopic measurements), may yield the standard free energy for adsorption; the temperature dependence of this quantity then provides standard enthalpies and entropies. Chromatographic measurements also have been used to obtain 'surface partitioning coefficients' (Hartkopf and Karger, 1973; Hoff et al., 1993). Another approach (Donaldson and Anderson, 1999) considers the free energy for transferring one mole of species from either the gas or solution phase to the surface.

Several organic surface-active solutes have been treated this way over a range of temperatures, yielding values of ΔG^0, ΔH^0, and ΔS^0 for adsorption to the air-water interface. In general, there is reasonable agreement among the various methods (Hoff et al., 1993; Donaldson, 1999a; Donaldson and Anderson, 1999b; Mmereki et al., 2000; Roth et al., 2002) for values of adsorption enthalpies; values of the other thermochemical parameters are explicitly dependent on the choice of standard state. For compounds that are expected to be better solvated by water, the standard enthalpies of adsorption are different from those of vaporization, but are related to the infinite-dilution solvation enthalpies. These observations suggest that adsorption of gases to the water surface involves specific interactions, rather than the surface merely providing a site for condensation.

In addition to the challenges noted above, there are several areas were fundamental knowledge is simply not available. At this time, there are no quantitative experimental data describing thermochemical adsorption parameters for inorganic anions. The issues of specifying the surface standard state and determining activity coefficients for species adsorbed on water surfaces have been raised in only a handful of studies to date. The choice of standard state will influence the importance and magnitude of the activity coefficients, which quantify the departure from the "ideal" mixture, expressed in the dimensions of the standard state. In its most recent evaluation IUPAC (Crowley et al., 2010) recommends using a molar area of $A_0 = 3.74 \times 10^7$ m^2 mol^{-1} as suggested by Kemball and Rideal (1946). Other choices (either explicit or implicit) include the "unit concentration" standard state, 1 mol m^{-2}, the "unit surface pressure" standard state (1 mN m^{-1}) and the "unit mole fraction" standard state, in which the surfactant surface

coverage, θ, = 1. Regardless of which standard state is used, it is important to be aware that its choice will affect the values of the thermochemical parameters derived, so direct comparisons are not always possible between the various reports in the literature.

The presence of salts in aqueous solution may affect the ability of organic molecules to dissolve, through the salting-out effect. The salting-out effect refers to the decrease in aqueous solubility and increase in the activity coefficient of aqueous neutral nonpolar compounds by inorganic salts. Hardly any studies of this effect are present in the atmospheric literature. Demou and Donaldson (2002) reported that both hexanoic acid and 1-propanol display a reduction in their propensities to partition from the gas phase to the surface as salt concentration is increased. At the same time, the maximum surface excess of organic, Γ_i^{max}, determined for salt solutions was larger than that for pure water and increased with increasing salt concentration.

5. In Section 5.2.1 it is stated "The mass accommodation coefficient α of H2O vapor on ice is. . ." It should be pointed out that when dealing with solids it is not always possible to make the distinction between adsorption and mass accommodation. Discussion of uptake terminology applied to solids would fit well into Section 2.2. 6. It should be pointed out in the Introduction that although the workshop motivating this over view manuscript took place in April 2007, the information and references are brought up to 2010.

Response - Agreed. Uptake of trace gases on mineral dust substrates correspond to (Langmuir) adsorption because, among other factors, the substrate does not undergo chemical change upon adsorption of the trace gas. On the other hand, adsorption of trace gases on ice is more problematic as several (acidic) trace gases such as HCl, HBr and HI modify the interface, even at low concentration. The Langmuir adsorption model may or may not hold, in any case it is used as a useful approximation for parametrization purposes (see Introduction to the heterogeneous data sheets on the IUPAC website, http://www.iupac-kinetic.ch.cam.ac.uk/supp_info/NewHetIntroOct2009.pdf), knowing full well that it may not rigorously be applied in the case of an ice substrate. In any case, the surface mass accommodation coefficient α_s is meant here.

Anonymous Referee #3
Received and published: 17 June 2010
I commend the authors for a readable synthesis of the literature on this diverse area of heterogeneous chemistry and trace gas uptake to clouds and aerosols. The authors provide guidance to a broad audience on important ongoing issues therein and how best to move forward. The controversial topics, many of which remain unresolved, were treated in a balanced way- highlighting the confounding issues and discussing the reasons why such issues remain. The content is highly appropriate for this journal, and I recommend publication. My comments are fairly minor.

Response – We appreciate the reviewer's endorsement.

General Comments: I agree with other referees that an overview figure of the processes involved in uptake would be helpful to bring less familiar readers up to speed.

Response – Agreed. See response to Referee #2's first point above.

There seems to be an inconsistency among the use of Recommendations for Future Work sections – sections which I think are highly valuable. Some of the main topical discussions have recommendations that are embedded within the main topical discussion while some have an entirely separate section. I suggest each topical section is followed by a separate. "Recommendations for Future Work" section.

Response – We agree and have developed more consistency among these subsections and created several more, as listed below.
Section 4 – Molecular Dynamics Simulations

Recommendations for Future Work - Future work to understand trace gas uptake using molecular simulation methods will benefit greatly from advances in computing hardware and software. Almost all previous simulations of molecular processes at the air/liquid interface have relied on approximate analytical expressions for interaction potentials, which are fitted to experimental data. Advanced computing resources now enable reliable simulations of liquid interfaces using electronic structure methods to describe the molecular interactions (Kuo and Mundy, 2004; Mundy et al., 2008). Studies that use more reliable interaction potentials such as electronic structure methods will help to understand the influence of the interaction potential on the structure, energetics, and dynamics at liquid interfaces, and address criticisms (Davidovits et al., 2005; Worsnop et al., 2004a; Worsnop et al., 2004b) of previous simulation results. More work is also needed to bridge the gap between the molecular scale treated in simulations to the macroscropic scale of the experiments. Uptake of molecules by water droplets is a macroscopic process that is controlled by mass transport in the gas and liquid phases, and can be influenced by molecular-scale processes occurring at the vapor/liquid interface. Multi-scale models that accurately include molecular scale phenomena in continuum models are required to provide a clear understanding of molecular processes in the uptake phenomenon.

Davidovits, P., Worsnop, D.R., Williams, L.R., Kolb, C.E. and Gershenzon, M., 2005, Comment on "Mass accommodation coefficient of water: Molecular dynamics simulation and revised analysis of droplet train/flow reactor experiment". Journal Of Physical Chemistry B, 109: 14742-14746.
Kuo, I.F.W. and Mundy, C.J., 2004, An ab initio molecular dynamics study of the aqueous liquid-vapor interface. Science, 303: 658-660.
Mundy, C.J., Rousseau, R., Curioni, A., Kathmann, S.M. and Schemer, G.K., 2008, A molecular approach to understanding complex systems: computational statistical mechanics using state-of-the-art algorithms on terascale computational platforms - art. no. 012014. In: Stevens, R.L. (ed.), SciDAC 2008: Scientific Discovery through Advanced Computing: 12014-12014.
Worsnop, D.R., Williams, L.R., Kolb, C.E., Mozurkewich, M., Gershenzon, M. and Davidovits, P., 2004a, Comment on "gas-phase flow and diffusion analysis of the

droplet-train/flow-reactor technique for the mass accommodation process".
Journal Of Physical Chemistry A, 108: 8542-8543.

Worsnop, D.R., Williams, L.R., Kolb, C.E., Mozurkewich, M., Gershenzon, M. and Davidovits, P., 2004b, Comment on "The NH3 mass accommodation coefficient for uptake onto sulfuric acid solution". Journal Of Physical Chemistry A, 108: 8546-8548.

For subection 5.1.1 Laboratory measurement of uptake of water onto water surfaces, subsection 5.1.3 Trace gas uptake on water surfaces, as well as subsections 5.1.4. 5.1.5, 5.1.6 and 5.1.7 "Recommendations for Future Work" will be tagged to last two paragraphs from subsection 5.1.3, amended, extended and reproduced below. A pointer to this material will be included at the end of each relevant subsection.

Recommendations for Future Work - Three major experimental challenges for uptake of water vapour and trace gases on pure water and aqueous solutions need further investigation. First, it is necessary to ensure that the experimental techniques that use large or moderate surface areas (e.g. wetted wall flow reactors, droplet train flow reactors, coaxial liquid jet reactors) do not underestimate uptake coefficients by improperly accounting for near surface gradients in trace gas concentrations due to finite gas phase diffusion rates. Second, it must be established that experiments that often approximate pure water uptake by employing acid or salt aqueous solutions to create and stabilize small droplets and achieve high surface to volume ratios (aerosol flow reactors, aerosol chambers) and techniques that dope aqueous solutions to overcome bulk Henry's law solubility constraints do not suffer from enhanced surface reaction and/or surface adsorption that mimic bulk mass accommodation. Third, techniques that involve rapid droplet growth (e.g. expansion cloud chambers) or rapid droplet evaporation (e.g. injection of free jets or droplet trains into near vacuum environments) must assure that their measurements and/or analysis methods accurately account for both the rapid interfacial mass transport and heat flux rates involved and that their experimental interfacial structural properties are not significantly different from the near equilibrium interfacial surfaces that are relevant for atmospheric gas uptake and evaporation processes.

Generally, reliable determination of uptake and accommodation coefficients requires approaches that, on one hand, decouple the thermodynamic equilibrium properties from kinetic properties and, on the other hand, account for the simultaneous mass and heat transfer related to condensation and evaporation. From an experimental perspective, well-defined gas phase composition and temperature profiles are among the key factors defining useful approaches.

We also recommend that attention be increasingly given to measurements in the field that can be used to demonstrate heterogeneous chemistry on real aerosol. In that regard, we highlight the early, ground-breaking efforts to measure the uptake coefficients of N2O5 on tropospheric aerosol (Brown et al., 2006; Bertram et al., 2009) and the first attempts to measure the effects of OH heterogeneous oxidation of tropospheric aerosol (George et al., 2008).

Added references:

1. Brown SS, Ryerson TB, Wollny AG, Brock CA, Peltier R, Sullivan AP, Weber RJ, Dube WP, Trainer M, Meagher JF, Fehsenfeld FC, Ravishankara AR, Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-70 (2006).
2. Bertram TH, Thornton JA , Riedel TP, Middlebrook AM, Bahreini R, Bates TS, Quinn PK, Coffman DJ, Direct observations of N2O5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, L19803 (2009).
3. George, I, J. Slowik, J.P.D. Abbatt, Chemical aging of ambient organic aerosol from heterogeneous reaction with hydroxyl radicals, Geophys. Res. Lett., 35, L13811 (2008).

Section 5.1.2 Field determination of uptake of water onto water surfaces

Recommendations for Future Work - While it is undoubtedly difficult to directly infer mass accommodation coefficient of water vapour on pure water by reconciliation of cloud droplet number with CCN using conventional coupled models of mass and heat flux, more comprehensive efforts now offer promise to quantify kinetic limitations. Mapping of offline molecular level quantification of aerosol composition onto online size-resolved broad composition measurements, along with measurements of mixing state by hygroscopicity can all be provided by modern comprehensive experiments. Such data can provide input for a model including other potential limitations on the kinetics of condensation (possible film formation at a known organic composition, for example). Careful measurements of droplet microphysics and updraught velocity together with selection of case study clouds eliminating non-adiabatic conditions have the promise to provide constraint on the kinetic parameters included in such a model.

Subsection 5.1.7 Role of organic coatings on aqueous surfaces

The last three paragraphs of section 5.1.7 will be designated as reproduced below.

Recommendations for Future Work - The effect of organic surface films on the uptake of a wider range of trace gases, including other organics, should be determined. Further studies should examine the effect of surface concentration and chemical content of organic films, as well as the effect of layer thickness of surface-active compounds on uptake. If possible, surface structure should be determined. Continued development of the PRA model or equivalent approaches to reliably represent the impact of organic films on trace gas surface adsorption, bulk absorption and the production and subsequent evaporation of both surface and bulk phase reactions.

Although there have been some field studies indicating an effect of ambient aerosol on N_2O_5 levels in the troposphere, its uptake on realistic atmospheric PM remains unclear. In particular, combined studies of trace gas removal and particulate composition will allow the partitioning of trace gases and their products to be better quantified. There is also a need for an increased input from the field measurement community to better quantify the composition and mixing state of the atmospheric aerosol particles.

The uptake of H_2O_2 offers another benchmark system for future study. The bulk kinetics of this system are comparatively well understood and will provide an important point of contact between the experimentalist community and the Pöschl, Ammann and Rudich model framework.

Sections 5.1.1 and 5.1.2 already have paragraphs marked for future work. The same title marking will be used as in the other subsections.

New Recommendations for Future Work paragraphs will be prepared for subsections 5.3 and 5.4 by revising and extending some of the current text.

A paragraph on future recommended work for subsection 5.5 Photochemistry on atmospheric surfaces is shown below.

Recommendations for Future Work - The impact of light on atmospheric chemistry has been studied for a long time and especially considered in atmospheric sciences through its ability to break bonds (i.e., photolysis). Recently, it has been recognized that HULIS, a term used to describe high molecular weight, partially chromophoric organic material with some similarity to humic soil components, constitute an important fraction of organic matter in tropospheric aerosols. Therefore, it should be interesting to consider the impact of light on chemical aging of an aerosol. While the existence of HULIS is now certain, atmospheric chemistry is still mostly unexplored. In this context, some of the fundamental unanswered questions are:

Which photochemical processes occur in the atmosphere and how do they modify the optically absorbing organic component of the aerosols?
Can those processes constitute an alternative pathway for oligomer formation?
How can these processes affect the photo-oxidant budget?
What is the role of adsorbed water on these chemical transformations?

Recent field-based or "real – air" measurements of reactive uptake, e.g. of N2O5 and heterogeneous processing, both direct and indirect, get little mention here but provide important insights for designing future laboratory studies (Brown, et al Science 2006; Brown, et al JGR 2009, George, et al GRL 2008, Bertram, et al GRL 2009)

Response – A reasonable point. A short paragraph citing these three pioneering studies and endorsing further similar field studies is included in the Recommendations for Future Work section associated with the report subsections covering uptake on aqueous aerosols.

Minor Comments

11172, line 25 – Sentence starting Laaksonen . . . seems redundant

Response - We do not agree that the sentence, which actually ends with a citation to (Laaksonen et al., 2005), is redundant. We have added an explanatory phrase: "and any discrepancy in droplet closure experiments must therefore be attributed to some other

suppression of growth kinetics not incorporated in the accommodation coefficient."

11173, line 1 – use of the word "real" in ". . .some other real suppression. . ." seems to imply that the films are not a real possibility.

Response - **The use of "real" is not meant to imply that films are not a real possibility. The phrase "…other real suppression…" is meant to distinguish it from the real suppression resulting from the presence of film forming components (as opposed to apparent suppression arising from inaccurate measurements of cloud CCN, droplet or water vapor properties).**

11174, lines 5 – 25; Even if there is an enhancement in the net uptake due to enhanced surface reactivity, such modifications of bulk reactivity ultimately provide an upper-limit to the bulk accommodation process, no? I would think such limits are still potentially useful for constraining models. I agree if interpreted as a "typical" gamma value it can cause problems. My point is to perhaps also acknowledge such limiting information can be useful but needs to be incorporated with care. In more than one location the word "that" appeared where it should be "than", e.g. 11177 line 9.

Response – We were not hypothesizing modifications of bulk reactivity, merely noting that enhanced surface reactivity due to reactive interfacial ions are a loss mechanism that can operate in parallel with bulk mass accommodation (and possible bulk reaction). We are merely warning that the total uptake may be the sum of two processes and should not be attributed to mass accommodation without showing that surface reaction is not a significant competitive sink for the gaseous species of interest.

"that" will be changed to "than" on page 1177, line 9.

Starting line 18, 11178 – discussion suggests behavior of N2O5 uptake consistent with mass accommodation limitation – prior to and after this discussion the potential for surface reactions with H+, and halide ions are indicated as a potential modification to bulk accommodation. Is that not the case here because the observed rate remains the same in most cases, but products change?

Response – While there is potential modification to bulk accommodation via surface reactions, we do not believe that we know enough about this reaction to say conclusively that some degree of surface reaction is occurring. We have added to the revised text (Line 6, p 11179) the following: "It is unknown the degree to which surface reactions compete with bulk reaction."

11186 lines 14 – 17 not a sentence

Response – Sentence amended to read:

Continued development of the PRA model (Poschl et al., 2007) or equivalent approaches is required to reliably represent the impact of organic films on trace gas surface adsorption, bulk absorption and the production and subsequent evaporation of both

surface and bulk phase reactions.

11186 lines 18 – 19 some references should be provided here

Response – Sentence amended to read:

Although there have been some field studies indicating an effect of ambient aerosol on N2O5 levels in the troposphere (Brown et al., 2006; Brown et al., 2009 and Bertram et al., 2009), its uptake on realistic atmospheric PM remains unclear.

References cited:

Brown et al., 2009 as in manuscript

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Direct observations of N2O5 reactivity on ambient aerosol particles, T.H. Bertram, J.A. Thornton, T.P. Riedel, A.M. Middlebrook, R. Bahreini, T.S. Bates, P.K. Quinn, D.J. Coffman. Geophysical Research Letters, 36 (2009), L19803, doi:10.1029/2009GL040248

11186 lines 24 on, an entire discussion of H2O2 uptake seems to be missing, did the authors mean HO2 here?

Response – We did not mean HO_2, and do not feel that the point can be usefully expanded upon without a long digression. We will amend this paragraph to read:

The uptake of H_2O_2 offers another benchmark system for future study. There are indications that its reactivity towards aerosol is strongly dependent on both relative humidity and aerosol composition (Pradhan et al., 2009). In addition, the bulk kinetics of this system are comparatively well understood and will provide an important point of contact between the experimental community and kinetic modeling frameworks.

11195 lines 13 – 24. The language here about aerosol flow tubes seems inconsistent with what follows where it is rather strongly recommended that aerosol flow tubes be used to study mineral dust particles in future experiments. I don't recommend making conclusions about what reactions can and cannot be studied in one apparatus as opposed to another. Each apparatus (flow reactor, static chamber, Knudsen, etc) has limitations that can or cannot be overcome depending on the instrumentation (accuracy and precision), creativity of the user, problem being studied, etc.

Response – We do not fully agree with the referee. A publication like the present one is exactly the place to make choices, based on the critical review of the published literature.

We do agree that every experimental technique has its advantages and disadvantages, which should clearly be identified and exhibited in a publication like this one. However, for the problem at hand, namely the investigation of the heterogeneous reactivity of airborne particles in the presence of atmospheric trace gases, the aerosol flow tube (AFT) technique seems to be the method of choice. Agreed, the present studies would not have been possible without prior information stemming form the application of coated-wall flow tubes (CWFT) and Knudsen flow reactors because everything is much harder to do in a CWFT; including determining the rate laws, reaction products, both gas and condensed phase, mass balances, temperature dependence, etc. The community's recent decision to apply AFT techniques for solid particle studies seems to be based on broad consensus that was reached during the Galway ACCENT Conference in 2007, from which the present paper evolved.

11196, lines 10 and on. Initially, I thought the authors were going to avoid discussing the actual kinetics, gammas, etc. This discussion should not be in a section entitled "outstanding issues and future work". At the very least the word "kinetics" should appear somewhere in the title to that section. This comment is also related to the general comment above about the "future work" sections not being consistent in scope or content. I suggest separating the review of the kinetics followed by a section on recommendations for future work.

Response – We agree with the referee that the sections on "future work" are not consistent throughout the manuscript. As shown above, we have made a significant effort to make them more consistent from one section to another for the final document. Regarding the data on pg. 11196, they just serve to illustrate a point, namely the disparate results of apparently identical chemical systems in terms of the uptake of trace gases on mineral dust. These data are not meant to represent a comprehensive discussion as done for instance on the IUPAC website (http://www.iupac-kinetic.ch.cam.ac.uk/). This paper is not designed to engage in a comprehensive review and evaluation of the kinetic results of heterogeneous reactions of atmospheric relevance; we do cite the IUPAC and NASA/JPL evaluation products where appropriate.