MASS-TRANSPORT CONSIDERATIONS PERTINENT TO AQUEOUS PHASE REACTIONS OF GASES IN LIQUID-WATER CLOUDS

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ABSTRACT.

Reactions of gases in liquid-water clouds are potentially important in the transformation of atmospheric pollutants affecting their transport in the atmosphere and subsequent removal and deposition to the surface. Such processes consist of the following sequence of steps: Mass-transport of the reagent gas or gases to the air-water interface; transfer across the interface and establishment of solubility equilibria locally at the interface; mass-transport of the dissolved gas or gases within the aqueous phase; aqueous-phase chemical reaction(s); mass-transport of reaction product(s) and possible subsequent evolution into the gas-phase. Description of the rate of the overall process requires identification of the rate-limiting step (or steps) and evaluation of the rate of such step(s). Identification of the rate-limiting step may be achieved by evaluation and comparison of the characteristic times pertinent to the several processes and may be readily carried out by methods outlined herein, for known or assumed reagent concentrations, drop size, and fundamental constants as follows: gas- and aqueous-phase diffusion coefficients; Henry's law coefficient and other pertinent equilibrium constants; interfacial mass-transfer accommodation coefficient; aqueous-phase reaction rate constants(s). A graphical method is described whereby it may be ascertained whether a given reaction is controlled solely by reagent solubility and intrinsic chemical kinetic or is mass-transport limited by one or another of the above processes. In the absence of mass-transport limitation, reaction rates may be evaluated uniformly for the entire liquid-water content of the cloud using equilibrium reagent concentrations. In contrast, where appreciable mass-transport limitation is indicated, evaluation of the overall rate requires knowledge of and integration over the drop-size distribution characterizing the cloud.

NATO ASI Series, Vol. G6
Chemistry of Multiphase Atmospheric Systems
Edited by W. Jaeschke

1. INTRODUCTION

A major emphasis of current atmospheric research is directed to acquiring an understanding of the processes giving rise to the composition of liquid-water clouds. Such research is motivated by the desire to understand the role of clouds in the cycling of atmospheric constituents and more specifically the role played by clouds in the delivery of soluble substances to the surface in precipitation.

The present paper focuses on the reactive uptake of gaseous substances by liquid-water clouds. Such reactive uptake has been implicated in field studies of the chemical composition of clouds (Lazrus et al., 1983; Daum et al., 1984) that have shown higher concentrations of aqueous sulfuric and nitric acids than can be accounted for by dissolution of soluble particulate matter present in clear air. The importance of in-cloud reaction of sulfur and nitrogen oxides is suggested as well on thermochemical and chemical-kinetic grounds (e.g., Schwartz, 1984a; Martin, 1984). Moreover, clouds, by their very nature, i.e., consisting of highly dispersed small droplets suspended in air, would appear to be an ideal reaction medium for promoting interphase mixing necessary for gas-aqueous reactions. These observations suggest that rates of uptake of gases by cloud droplets and of aqueous-phase reaction can be evaluated on the basis of thermochemical and chemical-kinetic considerations, provided appropriate account is taken of the rates of mass-transport processes within each of the two phases and at the interface. The objective of this paper is to outline methods for carrying out such evaluations, with emphasis on the mass-transport processes. These methods facilitate evaluation of the rate of aqueous-phase reactions in clouds and in turn of the coupling of the chemical kinetics in the two phases, suitable for incorporation in numerical models.

In addition to development of such methodology, considerable insight may be gained regarding rate-controlling processes by defining and comparing the characteristic times of the several processes. As it turns out, frequently one or another process is rate controlling so that the rate of the overall process may, to good approximation, be treated as the rate of the controlling process, thereby simplifying the analysis. In particular, if mass-transport processes are sufficiently rapid compared to aqueous-phase reactions that mass-transport limitation is negligible, then the rate of the overall process is governed entirely by chemical kinetics. In this limit the rate of reactive uptake of the gas becomes independent of the drop-size distribution characterizing the cloud, leading to substantial simplification of the description. At the other extreme, for very rapid reactions, the rate of reactive uptake is controlled entirely by the rate of gas-phase mass transport, which is strongly dependent on cloud microphysical properties but only weakly dependent on the identity of the transported species. In order to facilitate identification of such situations, we develop readily applicable criteria to ascertain whether these situations obtain or conversely whether the more complete treatment is required.

In addition to the application of the methods presented here to description of atmospheric systems, it should be noted that these methods are applicable as well to interpretation of laboratory studies of reactions of gases with spherical drops. In particular, considerations such as the dependence of the observed reaction rate on drop size may indicate the presence and nature of mass-transport limitation in the system under investigation.

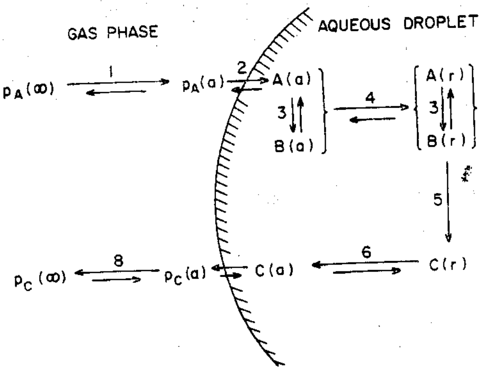

Figure 1. Schematic illustration of the sub-processes comprising the overall gas-aqueous reaction process under examination in this paper. Numbers labelling the several processes correspond to the listing presented in the text. A represents aqueous phase reagent species transferred from the gas phase; B, species in rapid equilibrium with A; and C, product species, at the surface of the drop (a) or in the interior (r); p_A and p_C represent gas-phase partial pressures of A and C at the surface of the drop (a) and at large distances from the drop (∞).

2. STATEMENT OF THE PROBLEM

In order to describe the overall process of a gas-aqueous reaction in a cloud, it is useful to consider this process as consisting of a sequence of steps or sub-processes. By achieving a description of the several sub-processes it becomes possible to describe the overall process. For this purpose we describe the overall process as consisting of the following sub-processes:

1. Gas-phase mass transport of the reagent gas (or gases) to the air-water interface.
2. Mass transport across the interface and possible establishment of solubility equilibria locally at the interface.
3. Establishment of rapid aqueous-phase equilibria involving the dissolved gas(es), e.g., hydration and acid-dissociation equilibria.
4. Aqueous-phase mass transport of the dissolved species within the droplet.
5. Aqueous-phase chemical reaction(s).
6. Mass transport of reaction product(s) in the aqueous phase.
7. Possible evolution of volatile product species into the gas phase.
8. Subsequent gas-phase mass transport of the evolved gaseous product.

These processes are illustrated schematically in Figure 1. The objective of this paper will be to describe these several processes and the coupling of these processes to constitute the overall process. The approach will be by means of description of the space and time dependence of species concentrations in terms of partial differential equations. We further restrict our consideration to problems characterized by spherical symmetry, in which the space dependence can be represented by the single radius variable r. Since most of the processes of concern have been treated, separately, by a variety of investigators in a variety of contexts (many are "classical" textbook examples), we make no apology for not solving the equations here, but merely state results (often by a figure) with appropriate citation.

A major reason for solving the time-dependent (i.e., partial) differential equation system is to discern the characteristic time for relaxation of transients. These "characteristic times" can often be surmised from dimensional considerations, although exact specification is arbitrary to a numerical factor of order unity. At times long compared to the characteristic time for a given process, the system reaches a "steady state" in which species concentrations, fluxes, reaction rates, etc., no longer vary as a function of time. In this steady-state limit, species concentrations are represented by an ordinary differential equation in the radius variable r. Treatment in the steady-state limit greatly simplifies the description of the system and, additionally, provides much insight.

For the system of interest here, which consists of coupled sub-processes, approach to the steady state will be governed by the slowest of the several processes. However, for sub-processes having greatly differing characteristic times, the simplification afforded by the steady-state treatment nonetheless obtains, since the "faster" system(s) will rapidly adjust to changes imposed by the time variation of the "slower" system, i.e., they will "follow" the slower system. In practice, for cloud systems (in contrast to some laboratory studies) such quasi-steady-state situations will almost invariably be the rule, as the cloud itself relaxes slowly to externally imposed conditions, e.g., adiabatic cooling imposed by lifting that leads to condensational growth of cloud droplets.

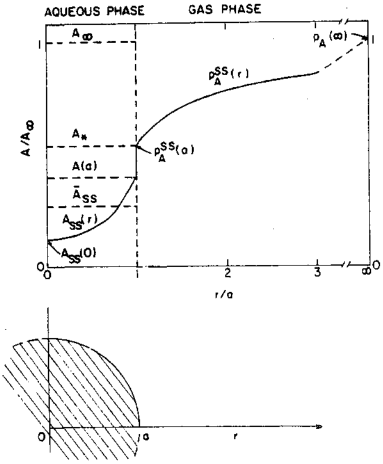

Figure 2. Hypothetical concentration profiles in gas and aqueous phases indicating gradient in reagent concentration due to flux of material into and within drop. Concentration scales of aqueous phase ($r < \underline{a}$) left ordinate and gas-phase ($r > \underline{a}$) right ordinate are chosen so that the same coordinate on each scale represents the condition of phase equilibrium. Departure from the uniform profile at the "bulk" ($r = \infty$) value represents the inability of mass transport to maintain the reagent concentration as the reagent is consumed by aqueous-phase reaction. After Schwartz and Freiberg (1981).

A schematic illustration of the spatial dependence within and in the vicinity of a single drop of the steady-state concentration of a gas undergoing aqueous-phase reaction is shown in Figure 2. Here the region $r > \underline{a}$ represents the gas phase surrounding the drop and the region $r < \underline{a}$

represents the interior of the drop. The scales representing aqueous concentration (left ordinate) and gas-phase partial pressure (right ordinate) are chosen such that equilibrium at the interface is represented by the same coordinate on each scale. For reactive uptake of the gaseous reagent negative departure from the uniform profile (at a value corresponding to the large-radius or "bulk" concentration) may occur in either or both of the two phases and/or at the interface because of the inability of mass-transport to maintain the uniform profile in the face of the aqueous reaction sink. For reaction higher than zeroth order in the dissolved reagent (i.e., essentially all cases of interest), this negative departure from a uniform profile results in a decrease in the reaction rate from that characteristic of a uniform profile, i.e., there is mass-transport limitation to the rate of reactive uptake of gas.

A second motivation for introducing the characteristic times of the several processes is that by appropriately comparing these quantities it is possible to discern whether the system, at steady state, is mass-transport limited and to identify the limiting process, or, alternatively, to establish that the rate of the overall process is governed by aqueous-phase chemical kinetics. This approach was introduced in earlier papers from the author's laboratory (Schwartz and Freiberg, 1981; Freiberg and Schwartz, 1981; Schwartz, 1984a) that serve as the basis for much of the present paper.

The foregoing discussion has outlined what may be referred to as the microscale problem, determination of the time and space dependence of concentrations, fluxes, and reaction rates within and in the vicinity of a single drop. In order to describe the rates of these processes in actual or model clouds (the "macro-scale problem") it is necessary as well to take into account pertinent physical properties of the cloud, most importantly the liquid water content and the drop-size distribution. By considering the droplets that comprise the cloud to be non-interacting it is possible to adduce a description of the coupling of the chemical kinetics in the two phases. The importance of this coupling has been pointed out in recent work of Chameides and Davis (1982, 1983); see also the review by Chameides (1985) in this volume. Description of chemical kinetics in the coupled two-phase system is achieved by means of a set of ordinary differential equations in species concentrations in the two phases. The transfer of material between phases is treated by a formalism involving phenomenological mass-transfer rate coefficients whose definition takes into account the pertinent cloud properties. The resulting system of ordinary differential equations may, under certain conditions, be treated entirely like systems of coupled differential equations for a single-phase situation that are conventionally employed in the description of gas-phase or aqueous-phase chemical kinetics.

The next several sections treat the individual sub-processes that comprise the overall gas-aqueous reaction pertinent to liquid-water clouds. First, we set the scene with a brief description of the properties of liquid-water clouds. The next section treats gas-aqueous equilibria, in particular the Henry's law equilibrium between a gaseous species and its dissolved counterpart. In Section 5 we define several expressions for chemical kinetic rates in mixed phase systems generally as well as in clouds specifically and define the relevant characteristic times. In Section 6 we examine the mass-transport processes pertinent to gas-aqueous reactions in clouds, treating gas-phase and aqueous-phase mass-transport mechanisms as well as the mechanisms of transport across the interface. Section 7 examines the kinetics of these mass-transport processes and develops expressions for evaluation of mass-transport limitation. In Section 8 these results are applied to develop a formalism for describing coupled gas-aqueous reaction systems in clouds.

3. CLOUD MICROPHYSICAL PROPERTIES

We confine this discussion to a bare-bones description of physical properties of liquid-water clouds pertinent to description of gas-aqueous reactions. For a more complete description the reader is referred to appropriate monographs (Pruppacher and Klett, 1978, pp. 9-21; Rogers, 1979, pp. 87-29; Mason, 1971, pp. 92-121).

Liquid Water Content.

The liquid water content is a key property of a cloud, governing the partition of a gas between gaseous and aqueous phases. The liquid water content of clouds ranges from one-tenth to several cm^3/m^3, typically 0.3 to 1 cm^3/m^3, or 0.3 to 1 parts per million by volume (Clouds are mostly air!). In description of partition of material and of gas-aqueous kinetics, it is convenient to express the liquid water content as a dimensionless volume fraction, L, typically $(0.3 \text{ to } 1) \times 10^{-6}$.

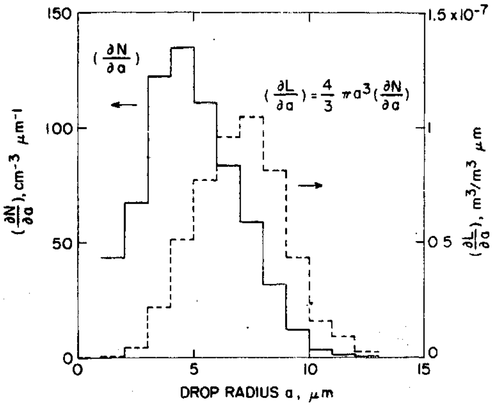

Figure 3. Spectra of droplet number density and volume fraction for continental cumulus. $N = 700\ cm^{-3}$; $L = 0.51 \times 10^{-6}$. Data of Knollenberg (1981).

Drop-Size Distribution.

The distribution of drop sizes within a cloud exerts a major influence on the kinetics of mass-transport processes within clouds. Observed cloud-droplet size distributions dN/da are typically rather narrow, peaking at some low value (below 8 µm diameter) and decreasing rather strongly with increasing size. (Drop sizes are most commonly referred to by diameter, but algebraic expressions, spectra, etc., are frequently given as a function of radius a, a convention we retain here.) Examples of measured cloud droplet size distributions are presented in Figures 3 and 4. For other examples see, e.g., Pruppacher and Klett (1978, pp. 10-21) and Mason (1971, pp. 98-113). The total number of drops per unit volume is given as the integral over the number distribution,

$$N = \int \left(\frac{dN}{da}\right) da .$$

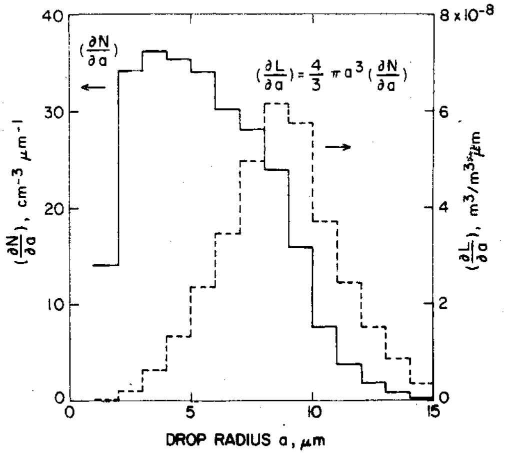

Figure 4. Spectra of droplet number density and volume fraction for aged stratus. $N = 300\ \mathrm{cm}^{-3}$; $L = 0.34 \times 10^{-6}$. Data of Knollenberg (1981).

In addition to the number density distribution it is also useful, particularly in the context of aqueous-phase reactions, to examine the distribution of liquid water content as a function of drop size,

$$\frac{dL}{da} = \frac{4}{3}\pi a^3 \frac{dN}{da} ,$$

also shown in Figures 3 and 4. Because of the greater volume of the larger droplets, the distribution of liquid-water content peaks at diameter values substantially greater than the number distribution. The liquid-water content is given as the integral over the partial volume distribution,

$$L = \int \left(\frac{dL}{da}\right) da = \frac{4}{3}\pi \int a^3 \left(\frac{dN}{da}\right) da .$$

Examination of representative cloud drop spectra permits us to bound the size range of drops concern in examination of gas-aqueous reactions in clouds. We take this range to be roughly 1-30 µm radius or 2-60 µm diameter.

It is of interest to consider the mean separation of cloud droplets $N^{-1/3}$, relative to the dimension of these droplets, to examine the adequacy of treating cloud droplets as non-interacting. For a "monodisperse" cloud of radius a

$$L = N \frac{4}{3}\pi a^3$$

whence

$$N^{-1/3} = (\frac{4\pi}{3})^{1/3} L^{-1/3} a = 1.61 L^{-1/3} a.$$

For $L \approx 10^{-6}$, $N^{-1/3} \approx 10^2$ a. The large interdrop spacing relative to drop size supports the model whereby gas-aqueous reactions in a cloud are treated as the summation of the processes taking place in the vicinity of and within non-interacting drops.

It is often convenient to represent the cloud drop-size distribution by an algebraic expression. One convenient such representation is that of Khrigian and Mazin (see Pruppacher and Klett, 1978, pp. 11),

$$\frac{dN}{da} = A\ a^2\ e^{-Ba}$$

where A and B are parameters that may be adjusted to match the mean drop radius $\bar{a}$ and liquid water volume fraction L, viz.,

$$B = 3/\bar{a}, \qquad \text{and}$$

$$A = (\frac{3}{4\pi})\ \frac{3^6}{5!}\ L\ \bar{a}^{-6} \approx 1.45\ L\ \bar{a}^{-6}\ .$$

For this distribution

$$N = (\frac{3}{4\pi})\ \frac{2 \cdot 3^3}{5!}\ L\ \bar{a}^{-3} \approx 0.107\ L\ \bar{a}^{-3}\ .$$

For $L = 0.5 \times 10^{-6}$ and $\bar{a} = 5 \times 10^{-4}$ cm, $N = 430$ cm^{-3}. Model distributions such as this are useful for the insight that may be gained in modeling gas-aqueous reactions in clouds.

Sedimentation Velocities.

The gravitational sedimentation of cloud droplets is important in the present context because of the convective flows induced thereby and the possible resultant enhanced mixing rates in either the gas or aqueous phase. This sedimentation, of course, is ultimately responsible for collisional growth of droplets and the delivery of precipitation to the surface. The focus here, however, is on the implications for mass-transport.

A first approximation to the terminal sedimentation velocity of cloud droplets is given by Stokes law for flow of a sphere in a viscous medium (e.g., Pruppacher and Klett, 1978, p. 322),

$$U_\infty = \frac{2\ a^2\ g\ (\rho_w - \rho_a)}{9\ \eta_a} \quad \frac{2\ a^2\ g\ \rho_w}{9\ \eta_a} . \tag{3.1}$$

Here g is the gravitational constant, ρ_w and ρ_a are the densities of water and air, respectively, and η_a is the viscosity of air. Departures from the velocity are found at both ends of the drop-size range of concern here (Pruppacher and Klett, loc. cit.). At the low end an increase in velocity is caused by the departure from pure continuum flow; under atmospheric conditions this departure amounts to 17% for $\underline{a}$ = 1 um and 1% for $\underline{a}$ = 10 um. At the high end of the drop-size range the Stokes law overestimates actual sedimentation velocities as drag forces on the drop are increasingly influenced by the drop velocity; this departure amounts to -6% for $\underline{a}$ = 30 µm and -13% for $\underline{a}$ = 42 µm. Nonetheless, at least for first approximation the Stokes formula may be employed for evaluation of sedimentation velocities of cloud drops.

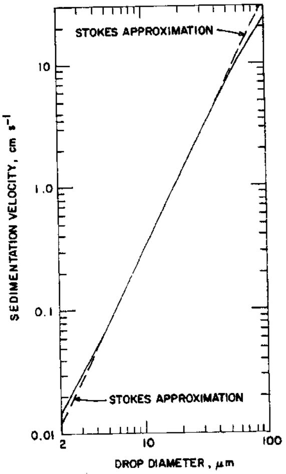

Figure 5. Droplet gravitational sedimentation velocity as a function of diameter. Departure from Stokes formula is indicated at both ends of the diameter range. Evaluated for 10 °C.

In evaluation of sedimentation velocities it is necessary to employ the viscosity of air. A convenient approximation is given by Pruppacher and Klett (1978, p. 323).

$$\eta_a(\mathrm{c.g.s.}) = (1.72 + 0.0049\ T) \times 10^{-4},\ T\ (^\circ\mathrm{C})\ .$$

The sedimentation velocity as a function of drop radius is shown in Figure 5.

Cloud Composition.

Measurements of the concentrations of dissolved constituents in cloudwater indicate, not surprisingly, a similarity in composition to that of rain (Daum et al., 1984, and references to earlier work therein). Principal cations are H^+ and NH_4^+; principal anions are $SO_4^=$ and NO_3^-, the distributions varying with location and altitude, as well as with time at any given location. Concentrations range from high values $\sim 10^{-3}$ equivalents/liter to substantially lower concentrations in remote locations. There is some indication of an inverse variation of concentration with liquid water content suggestive of dilution or concentration of non-volatile solutes associated with condensation or evaporation of water, respectively. Considerably higher concentrations of dissolved constituents (10^{-2} equivalents/liter or more) have been reported for ground fogs that are evidently characterized by rather low liquid water content (Munger et al., 1983).

The foregoing summary supports the approach adopted here of treating cloud water in the first approximition as sufficiently dilute to be treated as ideal solutions. However, it should be noted in situations where high accuracy is necessary that departures from ideality become appreciable (5 to 10 percent) at concentrations greater than 10^{-3} equivalents/liter (Adamson, 1973, p. 521).

Few measurements have been reported of concentrations of trace gases in interstitial air, i.e., the air in which the cloud drops are suspended. Evidently highly soluble gases (e.g., NH_3, HNO_3) are present at very low concentration consistent with rapid scavenging by cloud droplets (Daum et al., 1984). Gases of low solubility (e.g., O_3, NO_2) are commonly present within clouds, and occasionally appreceable concentrations of SO_2 are encountered.

Little is known as well about the concentration and composition of interstitial aerosol, i.e., particles present within clouds that have not been activated to become cloud drops. Several recent studies suggest that most but not all (by mass) of soluble aerosols present prior to cloud formation is rapidly (seconds to minutes) incorporated into cloud droplets by nucleation (Leaitch et al., 1983; Radke, 1983; Hegg and Hobbs, 1983). Measurements of the composition of the interstitial aerosol and comparison with corresponding cloudwater composition support this supposition (Daum et al., 1984). Presumably the non-nucleated interstitial aerosol is concentrated in the smaller size range, for which supersaturation sufficiently great to achieve nucleation has not been attained.

4. GAS-AQUEOUS EQUILIBRIA

A major consideration in describing mass transport and chemical kinetics of gas-liquid reactions is the equilibrium distribution of the reagent gas or gases between the two phases. For a detailed discussion of such equilibria pertinent to atmospheric gases, see the review by Warneck (1985) in this volume. For dilute solutions the distribution of a gas between the two phases is given by Henry's law, which states that the equilibrium concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas,

$$[X(aq)] = H_X p_X, \tag{4.1}$$

where H_X is the so-called Henry's law coefficient. A variety of units have been and continue to be employed for these several quantities. A particularly convenient set of units is p_X in atmospheres and $[X(aq)]$ in molar, consistent with the thermodynamic standard states chosen as 1 atm and 1 M, respectively, and H_X, therefore, in units of M atm^{-1}. H_X is thus seen to be the equilibrium constant of the reaction

$$X(g) = X(aq)$$

and is related to the difference in standard free energies of formation of the gaseous and aquated species as

$$H_X = \exp(-\Delta G^\circ / \underset{\sim}{R}T)$$

where

$$\Delta G^\circ = \Delta_f G^\circ[X(aq)] - \Delta_f G^\circ[X(g)] .$$

In the absence of specific chemical forces, Henry's law coefficients are fairly well correlated with the physical properties of solute and solvent. However, for polar, protic solvents (e.g., water) chemical forces frequently dominate, and Henry's law coefficients can differ greately for "similar" solutes. Examples of Henry's law coefficients of several atmospheric gases are given in Table 1. Henry's law coefficients generally increase with decreasing temperature, reflecting a negative enthalpy of solution.

In the case of gases which physically dissolve in water without further reaction the Henry's law coefficient may be measured directly, by allowing the system to reach equilibrium and measuring p_X and $[X(aq)]$. Similarly, in the case of a gas that establishes a solution-phase chemical equilibrium, e.g.,

$$SO_2(aq) = H^+ + HSO_3^-$$

$$HSO_3^- = H^+ + SO_3^=$$

the Henry's law coefficient may be determined from consideration of the several equilibria (e.g., Johnstone and Leppla, 1934). However, in the case of a gas that reacts rapidly and irreversibly to form much more highly soluble products, e.g., NO_2 to form NO_2^- and NO_3^-, the Henry's law coefficient can generally be determined only by indirect methods. Such methods include thermochemical cycles involving the aqueous-phase species (e.g., Schwartz

Table 1

Henry's Law Coefficients of Some Atmospheric Gases Dissolving in Liquid Water[a]

Gas	H, M atm^{-1}	Reference
O_2	1.3(-3)[b]	1
NO	1.9(-3)	1
C_2H_4	4.9(-3)	1
NO_2[c]	1 (-2)	2
O_3	1.3(-2)	3
N_2O	2.5(-2)	1
CO_2[d]	3.4(-2)	1
SO_2[d]	1.3	4
CH_3ONO_2[e]	2.6	5
PAN[c,e]	3.6	5
HNO_2	4.9(1)	6
NH_3[d]	6.2(1)	7
H_2CO	6.3(3)	8
H_2O_2	1 (5)	9
HNO_3[d]	2.1(5)	6

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a. T = 25°C except as noted.
b. The notation 1.3(-3) represents 1.3 x 10^{-3}.
c. Physical solubility; reacts with liquid water.
d. Physical solubility, i.e., exclusive of acid-base equilibria.
e. T = 22°C.

References: 1, Loomis (1928); 2, Schwartz and White (1983); 3, Briner and Perrottet (1939); 4, Johnstone and Leppla (1934); 5, Lee et al. (1983); 6, Schwartz and White (1981); 7, van Krevelen et al. (1949); 8, Blair and Ledbury (1925); 9, Martin and Damschen (1981).

and White, 1981; Schwartz, 1984b) and kinetic studies of the reactive uptake (e.g., Schwartz and White, 1983).

In considering the solubility of gases that undergo rapid reversible aqueous-phase reactions such as acid-base ionization equilibria, it is frequently convenient to extend the definition of Henry's law by defining a pseudo Henry's law coefficient that encompasses the totality of the dissolved species. For example, in the case of SO_2 we define

$$H^*_{S(IV)} \equiv [S(IV)]/p_{SO_2}$$

$$= ([SO_2(aq)] + [HSO_3^-] + [SO_3^=])/p_{SO_2}$$

$$= H_{SO_2}\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right) ,$$

where K_1 and K_2 are the first and second ionization constants of sulfurous acid. It is seen that $H^*_{S(IV)}$ so defined depends on the hydrogen ion concentration, and thus hat a linear relation between [S(IV)] and p_{SO_2} will obtain only for a solution that is adequately buffered compared to the incremental hydrogen ion contributed by the acid dissociation. Examples of pseudo Henry's law coefficient for some acidic and basic gases of atmospheric interest are shown as a function of solution pH in Figure 6. It is seen that the total amount of dissolved material may greatly exceed that dissolved by Henry's law alone, i.e., that H^* may greatly exceed H.

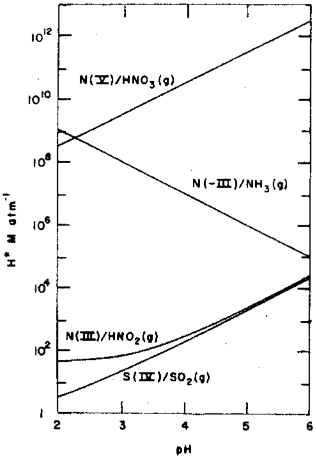

Figure 6. Effective Henry's law coefficients for gases which undergo rapid acid-base dissociation reactions in aqueous solution, as a function of solution pH. Buffer capacity of solution is assumed to greatly exceed incremental concentration from uptake of indicated gas. From Schwartz (1984a).

The equilibrium ratio of concentration of a species in the gaseous and aqueous phases is of particular importance in mass-transport considerations. This ratio is given according to Henry's law as

$$\frac{[X(aq)]}{[X(g)]} = \frac{H_X p_X}{p_X/\underset{\sim}{R}T} = H_X\underset{\sim}{R}T , \qquad (4.2)$$

where we have made use of the ideal gas law. For H_X in M atm^{-1} the universal gas constant R is taken as 0.082 atm M^{-1} K^{-1}, and $\underset{\sim}{R}T \approx 25$ atm M^{-1}. For a gas undergoing rapid aqueous-phase equilibrium, H_X must be replaced by H_X^*.

5. GAS-AQUEOUS CHEMICAL KINETICS

In view of the multi-phase nature of the system and of potential spatial nonuniformities, it is necessary to specify expressions for rates of chemical reactions with some precision. We restrict this discussion to reactions which occur in the aqueous solution phase. However, it is useful to express the reaction rate either in aqueous-phase units (M s^{-1}) or, for comparison to gas-phase rates, in equivalent gas-phase units (atm s^{-1}).

The local instantaneous aqueous-phase reaction rate R(a,r,t) is, in principle, a function of drop radius a, radius within the drop r, and for non-steady-state problems, of time t. It is this rate that is related, by a chemical rate law, to the local concentrations of reagents, catalysts, etc. we explicitly employ the chemical kineticist's convention of rate--moles (of reaction, as written) liter^{-1} second^{-1}, as distinct from that frequently employed in mass-transport discussions--moles (of reagent of interest) liter^{-1} second^{-1}. Thus for the reaction

$$2\ NO_2(aq) + H_2O \longrightarrow 2\ H^+ + NO_2^- + NO_3^- , \qquad [1]$$

$$R_1 = -\frac{1}{2}\frac{d_1}{dt}[NO_2(aq)] = \frac{d_1}{dt}[NO_3^-] .$$

The notation $\pm\, d_1 / dt\, [X]$ denotes the rate of increase/decrease of [X] due to reaction [1], i.e., the local flux of [X] through [1]. This would differ from the net rate of change in [X] if other processes were occurring simultaneously, e.g., other reactions or mass-transport processes. Lee and Schwartz (1981a) report a rate law for [1],

$$R_1 = k_1\ [NO_2(aq)]^2$$

by which they mean that the flux of NO_2(aq) through [1] is

$$\frac{d_1}{dt}[NO_2] = -2\ R_1 = -2\ k_1\ [NO_2(aq)]^2 .$$

For a reaction at steady state we may drop the explicit dependence on t and write R(a,r) or occasionally $R_{ss}(a,r)$.

The average rate over the droplet volume is given as

$$\bar{R}(a) = (\frac{4}{3}\pi a^3)^{-1} \int_0^a 4\pi r^2 \; R(a,r) \; dr \;. \qquad (5.1)$$

For a cloud characterized by a distribution of drop radii, the average rate, on a liquid water basis, is

$$\langle R \rangle = L^{-1} \int (\frac{4}{3}\pi a^3) \; (\frac{dN}{da}) \; \bar{R}(a) \; da \;. \qquad (5.2)$$

For a "mono-disperse" cloud $\langle R \rangle = \bar{R}(a)$.

It is often useful to express the reaction rate in partial pressure units, i.e., atmospheres (of reaction, as written) second^{-1}, which is evaluated as

$$(R) = L\underset{\sim}{R}T \; \langle R \rangle . \qquad (5.3)$$

Finally we introduce the fractional rate of removal of a gas-phase reagent X, having units s^{-1} (or commonly % h^{-1})

$$\rho_X = \nu_X (R) / p_X \;; \qquad (5.4)$$

here ν_X is the stoichiometric coefficient of X in the reaction as written.

Phase-mixed System.

It is instructive to consider these kinetic expressions in the limit of Henry's law equilibrium being satisfied. Reaction rates in this "phase-mixed limit", which are readily evaluated in terms of gas-phase reagent concentrations by means of the Henry's law solubility equilibria and aqueous-phase kinetic expressions, represent an upper-limit reaction rate, i.e., no mass-transport limitation. We consider initially a first-order reaction

$$R(a,r) = k^{(1)} \; [X(aq)](a,r) \;. \qquad (5.5)$$

Here we explicitly note that $[X(aq)]$ in principle depends on $\underline{a}$ and r; however, by assumption of Henry's law equilibrium,

$$[X(aq)](a,r) = H_X p_X \ , \tag{5.6}$$

the aqueous-phase reagent concentration is independent of $\underline{a}$ and r, and

$$\langle R \rangle = k^{(1)} H_X p_X \ .$$

In turn,

$$(R) = k^{(1)} \ L\underset{\sim}{R}T \ H_X \ p_X \ .$$

Finally, the fractional rate of reaction is

$$\rho_X = k^{(1)} \ L\underset{\sim}{R}T \ H_X \ .$$

Similar expressions obtain for situations other than simple first-order reaction of a single reagent. For example, the reaction of dissolved sulfur(IV) with H_2O_2,

$$S(IV) + H_2O_2 \longrightarrow S(VI) + H_2O$$

is characterized by a pH-dependent effective second-order rate constant:

$$R(a,r) = k^{(2)} \ [H_2O_2] \ [S(IV)] \ .$$

By assumption of Henry's law equilibrium for both species,

$$\langle R \rangle = k^{(2)} \ H_{H_2O_2} \ H^*_{S(IV)} \ p_{H_2O_2} \ p_{SO_2} \ .$$

The fractional reaction rates for the two reagents are

$$\rho_{SO_2} = k^{(2)} \ H_{H_2O_2} \ H^*_{S(IV)} \ L\underset{\sim}{R}T \ p_{H_2O_2} \ .$$

and

$$\rho_{H_2O_2} = k^{(2)} \ H_{H_2O_2} \ H^*_{S(IV)} \ L\underset{\sim}{R}T \ p_{SO_2} \ .$$

Similarly, in the case of second-order reaction of NO_2,

$$R(a,r) = k^{(2)} [NO_2(aq)]^2, \qquad (5.7)$$

$$\langle R \rangle = k^{(2)} H_{NO_2}{}^2 \, p_{NO_2}{}^2 \, , \qquad (5.8)$$

and

$$\rho_{NO_2} = 2 \, k^{(2)} \, H_{NO_2}{}^2 \, p_{NO_2} \, ,$$

where the factor of 2 represents the stoichiometric coefficient of NO_2 in [1].

Characteristic Time.

It is useful to define a characteristic time of aqueous-phase reaction that permits examination of mass-transport limitation by comparison to characteristic times of mass-transport processes. This can be defined on dimensional grounds as the ratio of the aqueous-phase concentration of a species X to the steady-state flux of X through reaction,

$$\tau_r = - [X(aq)] / \left(\frac{d_R[X]}{dt}\right)_{ss} = [X(aq)] / \nu_X R_{ss}(a,r) \, . \qquad (5.9)$$

For the H_2O_2-S(IV) reaction the effective first-order rate coefficients for reaction of S(IV) and H_2O_2 are

$$k^{(1)}_{S(IV)} = k^{(2)} [H_2O_2] \, . \qquad (5.10)$$

and

$$k^{(1)}_{H_2O_2} = k^{(2)} [SO_2] \, .$$

Similarly, for the NO_2-NO_2 reaction

$$k^{(1)}_{NO_2} = 2 \, k^{(2)} [NO_2 \, (aq)] \, . \qquad (5.11)$$

These quantities may be expressed in terms of gas-phase partial pressures by means of Henry's law equilibria.

For reaction by simple first-order kinetics,

$$\frac{d_R[X]}{dt} = -\ k^{(1)}[X]$$

such that

$$\tau_r = [k^{(1)}]^{-1}\ . \qquad (5.12)$$

i.e., the inverse of the first-order rate coefficient. For more complex rate expressions it is useful to define an effective first-order rate coefficient,

$$k^{(1)} = \frac{d_R\ [X]}{dt}\ /\ [X(aq)] \qquad (5.13)$$

such that τ_r continues to be represented by eq. (5.12).

6. MASS TRANSPORT PROCESSES

We outline here the pertinent processes responsible for mass transport separately in the gas and aqueous phases and across the gas-aqueous interface.

Gas Phase.

For systems with dimension much greater than the molecular mean free path ($a \gg \lambda$, or Knudsen number $Kn \equiv \lambda/a \ll 1$) mass-transport is considered to be adequately described as that of a continuum fluid, i.e., without explicit recognition of the motion of individual molecules (e.g., Hidy and Brock, 1970, p. 15). In air under standard conditions the mean free path is approximately 6×10^{-6} cm (0.06 μm) well less than the radius of cloud particles ($\gtrsim 1$ μm). Hence the mass transport of gas molecules to (or from) cloud droplets may be treated as a continuum process.

Transport of a reagent gas to a cloud droplet will occur at least at the rate governed by molecular diffusion, as augmented by any organized flows, e.g., turbulent motions of convection induced by the sedimentation velocity of the cloud droplet. Evaluation of the mass-transport rate as governed by molecular diffusion alone, therefore, yields a lower bound to this rate, and if no gas-phase mass-transport limitation is indicated by this rate, that conclusion holds a fortiori in the presence of organized flows. In fact, however, the influence of such flows relative to diffusion would appear to be minimal for the range of drop sizes characteristic of non-precipitating clouds.

To examine the importance of turbulence-enhanced mass transport, Brock and Durham (1984) note that the characteristic scale length of atmospheric turbulence is

$$r_t = (D_g{}^3 / \mathcal{E})^{1/4}$$

where D_g is the gas-phase diffusion coefficient and $\mathcal{E}$ is the turbulent energy dissipation rate. The criterion for the unimportance of turbulent mass transfer relative to diffusive is

$$a << r_t.$$

For $D_g \approx 0.1$ cm^2 s^{-1} and $\mathcal{E} = 10$ cm^{-2} s^{-3} (low atmospheric turbulence) or 10^4 cm^2 s^{-3} (intense turbulence), r_t = 0.18 and 0.018 cm, respectively, indicating appreciable turbulence-induced mass transport only for the larger drops at intense levels of turbulence. By this criterion we may neglect turbulence-induced mass transport in evaluation of gas-phase mass transport rates.

Convective mass-transport induced by droplet sedimentation is treated by Pruppacher and Klett (1978. p. 440 ff.) in terms of measured evaporation rates of falling droplets. For low Reynold number (Re < 2.5) the ratio of convective to diffusive mass-transport in air is approximated as 0.086 Re. Thus the criterion that convective mass transport not exceed 10% diffusive mass transport is satisfied for Re $\leq$ 1.16. This value of Reynold number correspond to a = 42 um (Pruppacher and Klett, 1978, p.326). Thus again molecular diffusion is seen to represent the major gas-phase mass-transport mechanism for droplets in the size range pertinent to clouds.

The gas-phase mass-transport of SO_2 to water droplets falling freely in air was modeled numerically by Baboolal et al. (1981) taking into account the flow field induced in the gas by the falling drop. Drop radii treated were 10, 71, 142, and 306 um. Significant enhancement of the steady-state uptake rate beyond that due to diffusion in stagnant air was found for all drop radii except 10 um. This enhancement amounted to approximately 50% at a = 71 um. For a = 40 um the enhancement would appear to be about 20% (Baboolal et al., 1981, Figure 2). It would thus appear that the treatment of gas-phase mass transport by diffusion alone yields a close approximation to the uptake rate throughout the size range of interest for liquid-water clouds.

Gas-Phase Diffusion Coefficients.

Measurements are available for the diffusion coefficients of a number of species of atmospheric interest in air, some which are listed in Table 2. (Since diffusion coefficients vary inversely with total pressure it is commonly the product P D_g that is tabulated.) It is seen that values of D_g (at 1 atm) are of the order of 0.1 $cm^2\ s^{-1}$, a value that we shall employ in examples treated below.

For gases whose diffusion coefficient in air has not been measured there are a number of closely related semi-empirical equations by which binary diffusion coefficients (including diffusion coefficients in air) may be estimated from the properties of the individual molecules. (For review see Sherwood et al., 1975, pp. 10-24; Marrero and Mason, 1982.) Lugg (1968) has compared the performance of 9 such equations for up to 147 compounds and found that the formula of Wilke and Lee (1955) yields a value within 5% of the observed value in 70% of the cases. A similar, somewhat easier to apply formula given by Fuller et al. (1966) also appears to yield good predictions for D_g.

The temperature dependence of the diffusion coefficient at 1 atm, at least for relatively narrow ranges of temperature, is given as

$$D_g \propto T^n$$

with values of n ranging from 1.5 to 2 (Chapman and Cowling, 1970, p. 264).

Aqueous Phase.

Mass transport within aqueous cloud droplets will, analogously to gas-phase mass transport, take place by molecular diffusion as enhanced by any organized flow. Such an organized flow may be induced by coupling of momentum from the relative motion of the falling drop within the air medium, and thus is increasingly important for larger drops. Pruppacher and colleagues (cf. Pruppacher and Klett, 1978, pp. 305-310) have examined internal circulation induced by droplet sedimentation and conclude, at least for smaller drops (< 100 um radius), that the Stokes-flow approximation accurately approximates the actual flow field. This approximation yields for the radial velocity within the drop

$$u_{ir} \approx \frac{\eta_a}{2\eta_w} U_\infty \left(\frac{r^2}{a^2} - 1\right) \cos \Theta \qquad (6.1)$$

where U is the terminal fall velocity of the drop, and n_a and n_w are the viscosities of air and water, respectively. Θ is the angle from the flow direction. In turn, from the expression (3.1) for U_∞

$$u_{ir} \approx \frac{g\ a^2\ \rho_w}{9\ \eta_w} \left(\frac{r^2}{a^2} - 1\right) \cos \Theta \ . \tag{6.2}$$

Equation (6.2) may be used to estimate the Peclet number characteristic of the system, which is a dimensionless index of the relative importance of convective to diffusive motion--Pe $\gtrsim$ 1 is indicative of significant convective mass transport (Brock and Durham, 1984)--

Table 2

Diffusion Coefficients of Some Representative Gases in Air

Gas	$P\ D_g$ atm cm^2 s^{-1}	Reference
H_2	0.712	1
He	0.687	2
H_2O	0.264	2
NH_3	0.234	3
CH_4	0.228	1
O_2	0.207	1
CO_2	0.159-0.170	1,2,3
HCOOH	0.153	4
CH_3OH	0.152	4
CH_3CH_2OH	0.118-0.133	2,4
Cl_2	0.128	3
SO_2	0.126	3
CH_3COOH	0.124	4
Br_2	0.094-0.106	3,4
CS_2	0.105	4

References: 1, Chapman and Cowling (1939). Data for 273K scaled to 298K as $T^{1.75}$; 2, Sherwood et al. (1975). Data for 313-317K scaled to 298K as $T^{1.75}$; 3, Andrew (1955). Data for 293K scaled to 298K as $T^{1.75}$; 4, Lugg (1968).

$$Pe = \frac{a\ u_{i\,r}(\max)}{D_a}$$

$$= \frac{g\ \rho_w\ a^3}{9\ \eta_w\ D_a}\ .$$

For a = 1, 10, 40 µm, Pe evaluated in this way has values 10^{-3}, 1, and 30, respectively, suggesting significant convective mass transport for a $\gtrsim$ 10 µm.

One additional point to be noted about equations (6.1) and (6.2) is the dependence of internal velocity on the viscosities of the two media, which reflects the mechanism of coupling of momentum between the two phases. As pointed out by Brock and Durham (1984) use of the bulk viscosity of water in these expressions assumes applicability of this quantity to the interface. This condition might not hold in the presence of a surfactant film (Gill et al., 1983), which would reduce the surface viscosity and thereby decrease the internal mixing from that evaluated using the bulk viscosity.

The mass transport of S(IV) within droplets having internal flow fields characteristic of drops falling freely in the atmosphere has been modeled by Baboolal et al. (1981). Drop radii treated were 10, 71, 142, and 306 µm. Significant enhancement of the aqueous-phase mass-transport rate over that due to diffusion alone as calculated for a stagnant drop was found for all drop radii except 10 µm. This enhancement amounted to approximately 50% at a = 71 um. It is not possible based on the data of the paper to estimate the enhancement for a = 40 um, but it would appear to be substantially less. This treatment would thus suggest that for the present it is appropriate to proceed with analysis of mass-transport rates based on molecular diffusion only, but with recognition that convective enhancement may be appreciable for a > 10 µm.

Aqueous-phase Diffusion Coefficients.

Diffusion coefficients of gases and other solutes in dilute solutions have been the subject of much study (Himmelblau, 1964; Wilke and Chang, 1955). Examples of some measured diffusion coefficients of dissolved gases are given in Table 3, and are seen to be $\sim 2 \times 10^{-5}$ $cm^2\ s^{-1}$ for many gases at 25 C. For simple solutes, i.e., solutes which do not undergo chemical reactions in solution, the semiempirical expression of Wilke and Chang (1955) gives a good estimate of the diffusion coefficient in terms of solute and solvent properties. In particular we note that there are two contributions to the temperature dependence,

Table 3

Diffusion Coefficients of Some Representative Gases in Water

Gas	D_a 10^{-5} cm^2 s^{-1}
He	5.8
H_2	3.4 - 4.1
N_2O	2.5
O_2	2.1 - 2.4
N_2	1.8 - 2.2
C_2H_2	2.0
SO_2	1.8 - 2.0
Ar	1.5 - 2.0
CO_2	1.8 - 1.9
Cl_2	1.4 - 1.7
CH_3Cl	1.5
H_2S	1.4

Source: Himmelblau (1964); T ≈ 25°C.

$$D \propto T\,\eta^{-1}$$

since the viscosity of solvents is generally temperature dependent. For water as solvent this viscosity has a temperature variation

$$\frac{\eta(T)}{\eta(25°)} = \exp\left[2140\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

that substantially exceeds the fractional variation in T.

In the case of solutes that dissociate into ionic constituents, e. g., $SO_2 = H^+ + HSO_3^-$, the diffusion coefficients of the ionic species may be calculated from the equivalent ionic conductivities $_i$ by the Nernst-Einstein relation (e.g., Adamson, 1973, pp. 546-547) as

$$D_i = \frac{\lambda_i RT}{z_i F^2}$$

where z_i is the ionic charge, and F is the Faraday constant; here $\underset{\sim}{R}$ is in joule mol^{-1} K^{-1}.

The ambipolar diffusion coefficient of the two ions (which must diffuse together) is

$$D = \frac{2\ D_1\ D_2}{D_1 + D_2} \ .$$

Diffusion coefficients of 1-1 electrolytes evaluated in this way are also of the order 2 x 10^{-5} $cm^2\ s^{-1}$.

Interfacial Mass Transport.

Despite the fact that for the total pressure and droplet size range characteristic of cloud gas-phase mass transport to (and from) cloud droplets is squarely in the continuum regime, nonetheless mass transport across the air- water interface, as across any interface is, ultimately, a process that involves individual molecules. Recognition of this principle, in conjunction with the kinetic theory of gases, permits the number of collisions of a gas-phase species X per unit interface area per unit time (the flux to the surface) to be evaluated as 1/4 $n_X\ \bar{v}_X$, where n_X is the number density of gas molecules and $\bar{v}_X$ is the average molecular speed (Hertz, 1882; Knudsen, 1913). In turn on a molar basis the collision flux is

$$\sigma_X^{coll} = \frac{1}{4}\ [X(g)]\ \bar{v}_X = \frac{1}{4}\ p_X\ \bar{v}_X/\underset{\sim}{R}T \ , \qquad (6.3)$$

where

$$\bar{v}_X = (8\ \underset{\sim}{R}T/\pi M_X)^{1/2} \ . \qquad (6.4)$$

Here M_X is the molar mass ("molecular weight") of species X; for M_X in g mol^{-1} and $\bar{v}_X$ in cm s^{-1}, $\underset{\sim}{R}$ has units erg $mol^{-1}\ K^{-1}$. This expression was initially applied to a discussion of condensation and evaporation rates of pure substances by introduction of a mass accommodation coefficient α representing the fraction of collisions resulting in condensation, yielding for the condensation flux

$$\sigma_X^{cond} = \frac{1}{4}\ \alpha\, p_X\ \bar{v}_X/\underset{\sim}{R}T \qquad (6.5)$$

As noted by Knudsen (1913) it is not possible a priori to specify the value of the accommodation coefficient. This point was underscored six decades later by Sherwood et al. (1975, p. 183), who observe that "Not only is there no useful theory to employ in predicting α, there is no easy way to experimentally measure it."

In the present context we are interested not so much in the self accommodation coefficient, as defined above, but in the accommodation coefficient of a solute gas impinging on a solvent, specifically water. However we note that equations (6.3) and (6.5) are applicable as well to partial pressure (specified for the interface) so that the formalism initially developed for condensation is applicable also to dissolution.

With respect to measurement we note that accommodation coefficients may be determined from measurement either of the uptake rate or of the evaporation or desorption rate, the latter by means of detailed balance arguments--at equilibrium the rate of evaporation is equal to the rate of condensation.

The values of reported accommodation coefficients vary considerably. In a number of studies with pure substances including metals (Knudsen, 1913; Langmuir, 1913), solid organic fatty acids and alcohols (Littlewood and Rideal, 1955) and liquid organics (Maa, 1967, 1970; Chang and Davis, 1976) the accommodation coefficient was determined to be unity. Other investigators, however, report values of α as low as 10^{-9} (see the discussion and references in Sherwood et al., 1975, pp. 182-184; also, Paul, 1962). Experimental difficulties associated with the measurements include both accurate knowledge of the surface temperature and maintenance of a surface that is free from surfactant films. It is suggested (Sherwood et al., 1975; Chang and Davis, 1976) that if both of these problems are resolved, the available data suggest that the evaporation coefficient or self-accommodation coefficient for liquids is essentially unity.

With respect to the self-accommodation coefficient of water there is a disquieting lack of agreement between investigators. Pruppacher and Klett (1978, pp. 133-135) summarize a number of these studies, reporting values of α ranging from ~ 0.01 to 1. In addition to the studies cited there one would call attention also to the work of Maa (1967, 1970), which reports $\alpha = 1$ for a study with a water jet, and of Wagner (1982) monitoring droplet growth in an expansion cloud chamber, also reporting $\alpha = 1$. Pruppacher and Klett observe that the data fall into two sets, noting that studies performed with rapidly renewed surfaces exhibit higher values of α (0.2 to 1). This distinction would be consistent with inhibition of mass transport at the interface in static experiments by unavoidable surfactant films. It should be noted that even monomolecular films can inhibit the evaporation rate from water surfaces (La Mer, 1962). It should also be noted that surfactant materials might be commonly present on atmospheric aerosols (Graedel et al., 1983) and thereby serve to inhibit mass transfer to cloud droplets formed from such aerosols. Pruppacher and Klett suggest that the condition of a rapidly renewed surface would be unlikely to be realized in clouds and propose that the lower values of α (0.01 to 0.07) be employed in cloud physics computations.

Relatively few studies have been performed examining the accommodation coefficient for uptake of solute gases by water. Danckwerts (1970, p. 69) suggest that there is no appreciable surface resistance for uptake of gases such as CO_2 by water, except in the presence of surfactants. However examinations of the papers cited by Danckwerts in support of this statement (Raimondi and Toor, 1959; Harvey and Smith, 1959) suggests that these studies were insensitive to values of α greater than perhaps 10^{-3}, although indeed a severe decrease in χ (to 6×10^{-6}) was indicated in the presence of surfactants (Harvey and Smith, 1959).

In summary, there is a growing body of information suggestive that the self accommodation coefficient of liquids approaches unity for clean surfaces. However relatively little information is available regarding the magnitude of the accommodation coefficient of potential reagent gases either on clean liquid-water surfaces or on surfaces of natural cloud droplets. For this reason we must treat α somewhat as an adjustable parameter and examine the sensitivity of mass-transport rates to the value of this quantity. As it turns out, for representative atmospheric conditions (as tested in Section 7), overall mass-transport rates are relatively insensitive to values $\alpha \geq 0.01$, but become increasingly sensitive to lower values of α. These observations suggest the importance of laboratory study of for various solute gases both on clean surfaces and on surfaces representative of natural clouds.

7. MASS-TRANSPORT KINETICS

In this section we examine the kinetics of mass-transport processes in the gas-phase, at the gas-water interface, and in the aqueous phase from the perspective of ascertaining the influence of mass-transport kinetics upon the overall rate of the gas-aqueous reaction. Specifically, it is the objective of this section to develop approaches to evaluating the departure of the overall rate from that which would obtain in the absence of mass-transport limitation as a function of the pertinent conditions--solubilities, rate constants, drop size, accommodation coefficient, reagent concentrations. This discussion thus focuses upon concentration profiles about and within a single drop of radius $\underline{a}$ (cf. Figure 2) leading to an evaluation of $\bar{R}(a)$ (as defined in equation 5.1). A secondary objective of the discussion is to define the conditions where mass-transport limitation is sufficiently small, say 10%, that the kinetics of the system may be approximated as phase-mixed. In this limit description of the kinetics is considerably simplified.

In this discussion we consider first gas-phase mass transport, then interfacial, and finally aqueous-phase. Mass-transport in both phases is assumed to occur only by molecular diffusion, as discussed in Section 6. Mass transport at the interface occurs by the mechanism of gas-kinetic collisions with arbitrary accommodation coefficient α.

The coupling of gas-phase and interfacial mass-transport kinetics to the rate of aqueous-phase reaction is entirely general, depending only on the reaction rate averaged over the drop, $\bar{R}$, i.e., independent of the details of the reaction mechanism. In contrast, the aqueous-phase mass-transport and kinetics are intimately coupled, and a different treatment is required for each mechanism for quantitative description of mass-transport limitation.

Happily, the case of a first-order reaction (or pseudo-first-order in diffusing species) is analytically soluble. We thus focus on the example of a first-order mechanism both for the quantitative results afforded for this mechanism and for the qualitative insights provided for other kinetic rate expressions.

Gas Phase.

We first consider gas-phase diffusion of a species to the surface of a drop, a problem initially treated by Maxwell (1877). In the absence of gas-phase sources or sinks, the differential equation for gas-phase concentration G in spherical symmetry is (e.g., Crank, 1975, p. 89)

$$\frac{\delta G}{\delta t} - D_g \frac{1}{r^2} \frac{\delta}{\delta r} (r^2 \frac{\delta G}{\delta r}) = 0 \ . \qquad (7.1)$$

We first consider a situation for which the concentration is initially uniform ($t \leq 0$) in which diffusion to a perfectly absorbing sphere of radius a is initiated at $t = 0$. The long-time (steady-state) solution to (7.1) is obtained by setting $dG/dt = 0$, which yields the ordinary differential equation

$$D_g \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{dG}{dr}) = 0 \qquad (7.2)$$

having solution (still for $G(a) = 0$)

$$G_{ss}(r) = G_{\infty} (1 - \frac{a}{r}) \ . \qquad (7.3)$$

The flux corresponding to this profile is

$$F_{ss}(r) = - D_g \frac{dG_{ss}(r)}{dr} = - D_g G_{\infty} \frac{a}{r^2} \ . \qquad (7.4)$$

At steady state the flux of reagent into the drop is equivalent to a reaction rate averaged over the drop as

$$\bar{R}_{ss} = -\left(\frac{4}{3}\pi a^3\right)^{-1} (4\pi r^2)\ F_{ss}(r), \tag{7.5}$$

whence, for G in mol/liter, we may equate the flux (7.4) to an average molar uptake rate

$$R^{(g)}_{\max} = \frac{3\ D_g\ G_\infty}{a^2}\ . \tag{7.6}$$

Here the superscript (g) denotes gas-phase mass transport and the subscript max denotes that the flux (7.4) for G(a) = 0 represents the maximum steady-state flux into the drop that can be achieved by gas-phase diffusion. In terms of gas-phase partial pressure

$$R^{(g)}_{\max} = \frac{3\ D_g\ p_A(\infty)}{\underset{\sim}{R}T\ a^2}\ . \tag{7.7}$$

This maximum uptake rate is shown as a function of drop diameter in Figure 7. It is seen that the maximum uptake rate, expressed per ppb of gas-phase reagent permits quite substantial reaction rates in the context of concentrations of cloudwater-dissolved materials, e.g., 5 x 10^{-5} M s^{-1} or 0.18 M h^{-1} at 10 μm diameter.

The recognition that there is a maximum rate at which material can be diffused into a

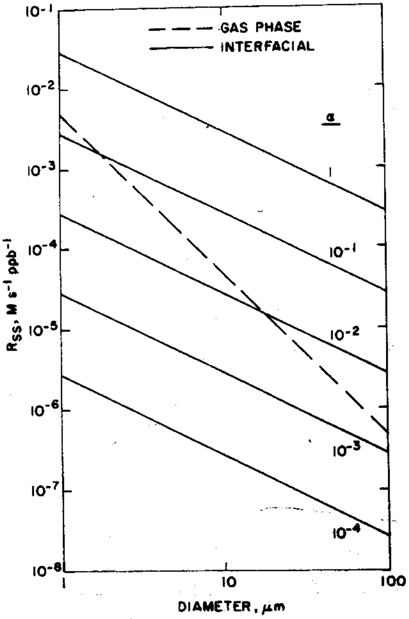

Figure 7. Maximum molar uptake rate per ppb of gas-phase reagent as a function of cloud drop diameter, as controlled by gas-phase diffusion (- - -) or interfacial collision rate (——) for indicated values of the accommodation coefficient α. Conditions: T = 298K, D_g = 0.1 cm^2 s^{-1}, M = 30 g mol^{-1}.

droplet leads to identification of an important characteristic time associated with gas-aqueous reaction, viz., the time constant associated with saturating the drop in the reagent gas in the absence of any aqueous-phase sink,

$$\tau_{\mathrm{sat}}^{(g)} = \frac{[A]_{\mathrm{eq}}}{R_{\max}^{(g)}} = \frac{H_A \underset{\sim}{R}T\ a^2}{3\ D_g}\ . \tag{7.8}$$

(For a gas such as SO_2 that undergoes rapid aqueous-phase equilibrium, H in (7.8) would be replaced by H*.) As shown by Freiberg and Schwartz (1981) this characteristic time was sufficiently great under the conditions of certain laboratory kinetic studies of the oxidation of S(IV) to have appreciably decreased the S(IV) concentration and in turn the oxidation rate from the steady-state values that had been assumed in the analysis of the kinetic data.

Identification of the characteristic time associated with saturating the drop by gas-phase diffusion permits us to anticipate a further condition that must be satisfied in order that the rate of reaction at steady state not be restricted by the rate of diffusive mass transport, viz., that the time required to saturate the drop be short compared to the characteristic time of reaction of the dissolved material, i.e.,

$$\tau_{\mathrm{sat}}^{(g)} << \tau_r\ . \tag{7.9}$$

This supposition is verified shortly.

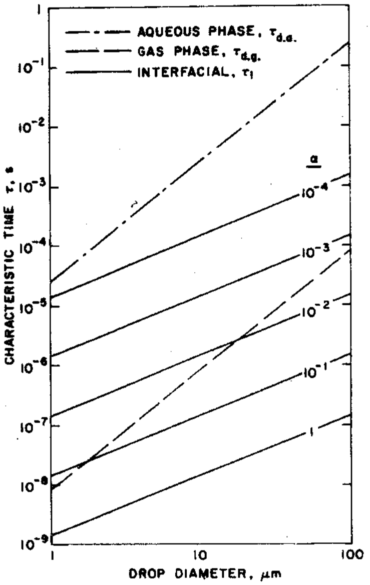

Figure 8. Characteristic times associated with diffusion in aqueous-phase ($\tau_{d.a.}$) and gas-phase ($\tau_{d.g.}$) and with interfacial mass transport (τ_i), as a function of diameter for a spherical droplet. Diffusion coefficients are 1×10^{-5} and 0.1 $cm^2\ s^{-1}$ for aqueous and gas phase, respectively; τ_i, evaluated for molecular weight 30, is shown for indicated values of the accommodation coefficient α.

We now return to the time-dependent equation. Based upon dimensional considerations, we anticipate the characteristic time for approach to the steady-state solution to be of order (a^2/D_g); we arbitrarily define the characteristic time associated with gas-phase diffusion as

$$\tau_{d.g.} = \frac{a^2}{3\ D_g}\ ; \tag{7.10}$$

this definition differs slightly from that introduced by Schwartz and Freiberg (1981). The characteristic time for gas-phase diffusion (as well as those for aqueous phase diffusion and for interfacial mass transport, to be introduced below) is shown as a function of drop diameter in Figure 8. The solution to the time-dependent problem has been given by various authors (e.g., Beilke and Gravenhorst, 1978; Seinfeld, 1980, pp. 76-79). One convenient way to depict this solution is as the flux into the drop as a function of time, Figure 9. This flux is initially quite high but asymptotically approaches the steady-state flux given by equation (7.4). In fact, the asymptotic approach to the steady-state flux is quite slow; nonetheless, as may be seen by comparison of the characteristic times of gas and aqueous diffusion in Figure 8, the relaxation of the gas-phase system is still sufficiently rapid that the gas-phase system may be considered to rapidly adjust to changes in conditions imposed by the aqueous phase system.

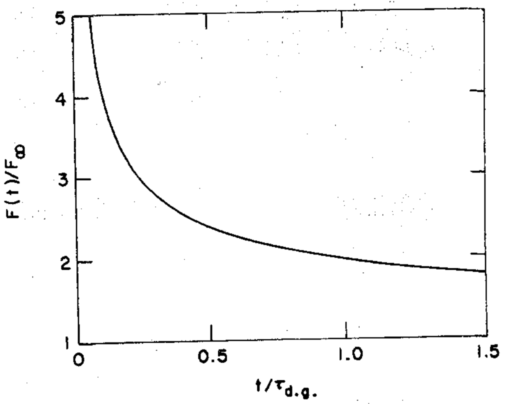

Figure 9. Time dependence of flux of gas into irreversible absorbing solution. Abscissa is expressed as dimensionless ratio of time to $\tau_{d.g.} = a^2/3D_g$; ordinate is expressed as ratio of flux to infinite-time value, $F_\infty = D_g G(\infty)/a$.

We now consider the steady-state equation (7.2) for arbitrary G(a), $0 \leq G(a) \leq G(\infty)$. The resulting concentration profile is (cf. Figure 2)

$$G(r) = G(\infty) - \frac{a}{r}\,[G(\infty) - G(a)] \ . \tag{7.11}$$

Equating the resultant flux with a rate of reactive uptake of A in the drop ν_A R(a), we obtain for the departure from uniform gas-phase concentration

$$G(\infty) - G(a) = \frac{a^2}{3D_g}\,\nu_A\,\bar{R}(a) \tag{7.12}$$

or, in terms of partial pressure

$$p_A(\infty) - p_A(a) = \frac{a^2 \underset{\sim}{R} T}{3\ D_g}\,\nu_A\,\bar{R}(a) \ . \tag{7.13}$$

Equation (7.13) permits us to formulate a criterion for absence of gas-phase mass-transport limitation, <u>viz.</u>,

$$\frac{p_A^{(\infty)} - p_A^{(a)}}{p_A^{(\infty)}} \le \mathcal{E}_g \ll 1 \ . \qquad (7.14)$$

This criterion sets an upper bound on the aqueous-phase reaction rate

$$\nu_A \bar{R}(a) \le \mathcal{E}_g \frac{3D_g}{a^2 \underset{\sim}{R}T} p_A^{(\infty)} \ . \qquad (7.15)$$

It is readily established that the bound (7.15) is equivalent to the intuitive supposition (7.9) for the absence of gas-phase mass-transport limitation.

The bound (7.15) may expressed in terms of solubility and rate coefficients for various mechanisms. For first-order kinetics (eq. 5.5, $\nu = 1$). We obtain the bound

$$k^{(1)} H_A \le \mathcal{E}_g \frac{3D_g}{\underset{\sim}{R}T \ a^2} \ . \qquad (7.16)$$

This inequality is illustrated in Figure 10 for various values of drop diameter for $\mathcal{E}_g$ arbitrarily taken as 0.1. In preparing this figure we have employed $D_g = 0.1$ cm^2 s^{-1}, taking advantage of the relative insensitivity of D_g to the identity of the diffusing gas, as illustrated in Table 2. For the coordinates of the figure taken as log $k^{(1)}$ and log H_A, the inequality (7.16) is represented by a region in the $k^{(1)}$--H_A plane below and to the left of the line representing the condition of equality. To employ Figure 10 the point ($k^{(1)}$, H_A) corresponding to a situation of interest is located on the figure. For a reagent gas undergoing rapid aqueous-phase equilibrium H^* must be employed. Similarly, for a second-order rate coefficient (5.10) must be employed. The point ($k^{(1)}$, H_A) is then compared to the location of the bound (7.16) for various drop sizes; for the point below and to the left of the line gas-phase mass-transport limitation to the rate of reaction does not exceed 10%.

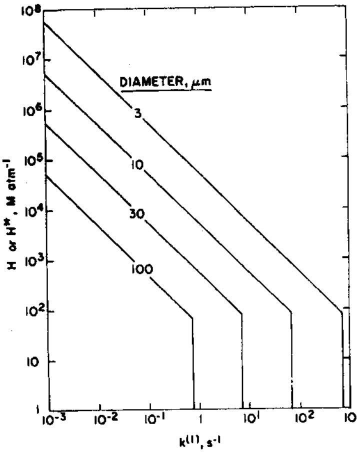

Figure 10. Gas-phase and aqueous-phase mass-transport limitation. The several lines represent the onset (10%) of mass-transport limitation for the indicated values of drop diameter. Diagonal sections represent gas-phase limitation; vertical sections represent aqueous-phase limitation. For situations such that ($k^{(1)}$, H) is below and to the left of a given line mass-transport limitation is less than 10% for the indicated drop diameter. Evaluated for $D_g = 0.1$ cm^2 s^{-1}, $D_a = 1 \times 10^{-5}$ cm^2 s^{-1}.

Figures such as this are useful (Schwartz, 1984a) as they permit a readily applicable means by which it may be ascertained that a situation of interest is free of mass-transport limitation or, conversely, that an evaluation of mass-transport limitation is required in an examination of the overall gas-aqueous reaction kinetics.

A similar treatment can be given for second-order kinetics (eq. 5.8, = 2), yielding

$$k^{(2)} H_A^2 \leq \mathcal{E}_g \frac{3\ D_g}{2\ \underset{\sim}{R}T\ a^2\ p_A} \ . \qquad (7.17)$$

It is seen that for other conditions held constant there may or may not be gas-phase mass-transport limitation depending on the reagent partial pressure. Example of second-order reactions of atmospheric interest include $2NO_2$ [+ H_2O (l)] $\longrightarrow$ $2H^+ + NO_2^- + NO_3^-$ (Lee and Schwartz, 1981b) and $2HO_2 \longrightarrow H_2O_2(aq) + O_2$ (Schwartz, 1984b).

Interfacial.

As discussed in Section 6, the kinetic theory of gases sets an upper limit to the flux of a gas to an interface. We note further that the effective flux of a reactive gas across this interface may be less than that given by the gas- kinetic collision rate, i.e., the accommodation coefficient for this mass transport may be less than unity. We examine here the limitation imposed by this finite rate of mass transport on the rate of uptake and reaction of gases in cloud droplets.

Following equation (6.5) we denote the effective flux of reagent species A from the gas-phase into the aqueous-phase of a droplet of radius a as

$$\sigma_+ = p_A(a)\ \bar{v}\ \alpha / 4\ \underset{\sim}{R}T \ . \qquad (7.18)$$

Here the subscript + explicitly denotes that this flux represents the gross (or one-way) flux into the drop. Also we explicitly employ $p_A(a)$, the partial pressure at the interface, which may not be approximately equal to the bulk partial pressure because of the gas-phase concentration gradient.

The flux (7.18) sets an upper limit to the rate of uptake of a gas by a droplet of radius a, exactly analogously to the maximum diffusive flux, equation (7.4), yielding for the maximum molar uptake rate

$$R^{(i)}_{max} = \frac{3\ p_A(a)\ \bar{v}\alpha}{4\ \underset{\sim}{R}T\ a} \qquad (7.19)$$

This maximum uptake rate is shown as a function of drop diameter in Figure 7 for various values of the accommodation coefficient α. Comparison of $R_{max}^{(i)}$ with $R_{max}^{(g)}$, the maximum uptake rate permitted by gas-phase diffusion, allows identification of which of these two mass-transport processes is more restrictive and therefore controlling. It is seen that for $\alpha \gtrsim 0.1$ gas-phase diffusion is more restrictive over the drop-size range of interest, whereas for $\alpha \lesssim 10^{-3}$ interfacial mass transport is more restrictive.

The recognition that there is a maximum rate of interfacial mass transport into a drop leads to identification of a characteristic time associated with saturating the drop in the reagent gas as controlled by interfacial mass transport (cf., $\tau_{sat}^{(g)}$, eq. 7.8) in the absence of any aqueous-phase sink,

$$\tau_{sat}^{(i)} = \frac{[A]eq}{R_{max}^{(i)}} = \frac{4\ H_A\ \underset{\sim}{R}T\ a}{3\ \bar{v}\,\alpha} . \tag{7.20}$$

Depending on whether $R_{max}^{(i)}$ or $R_{max}^{(g)}$ is controlling, the time to saturate the drop in the reagent gas will be controlled by $\tau_{sat}^{(i)}$ or $\tau_{sat}^{(g)}$, respectively.

Analogous to the argument above for gas-phase mass transport, identification of the characteristic time associated with saturating the drop by interfacial mass transport permits us to anticipate the condition that must be satisfied in order that the rate of reaction at steady state not be restricted by the rate of interfacial mass transport, viz., that the time required to saturate the drop be short compared to the characteristic time of reaction of the dissolved material, i.e.,

$$\tau_{sat}^{(i)} << \tau_r \tag{7.21}$$

This supposition is verified shortly.

We now wish to address the net flux across the interface, which will differ appreciably from the gross flux when the aqueous-phase concentration is appreciable. We observe that we may express the gross flux (7.18) equally well in terms of $[A]^*$, the aqueous-phase concentration of A in equilibrium with $p_A(a)$ as

$$\sigma_+ = [A]^*\ \bar{v}\,\alpha/4\ H_A\ \underset{\sim}{R}T\ . \tag{7.22}$$

The actual gross flux of material leaving the aqueous phase into the gas phase is given by the same expression but employing the actual aqueous-phase concentration at the surface instead of the equilibrium concentration,

$$\sigma_- = [A]_a\ \bar{v}\,\alpha/4\ H_A\ \underset{\sim}{R}T\ . \tag{7.23}$$

This is so because, by microscopic reversibility, σ_+ must equal σ_- at equilibrium and because the flux is linear in concentration. The net flux of material transfer into solution is

$$\sigma = \sigma_+ - \sigma_- = \frac{\bar{v}\,\alpha}{4\ H_A\ \underset{\sim}{R}T}\left(H_A\ p_A(a) - [A]_a\right)\ . \qquad (7.24)$$

This net flux may be equated to the rate of reactive uptake of A in the drop $_A\bar{R}(a)$ to optain the departure from Henry's law equilibrium at the surface that results from this uptake rate:

$$H_A p_A(a) - [A]_a = \frac{4a\ H_A\ \underset{\sim}{R}T}{3\ \bar{v}\ \alpha}\ \nu_A\ \bar{R}(a)\ . \qquad (7.25)$$

The difference between $H_A p_A$ and $(A)_a$ is represented by the step in concentration profile at the interface indicated in Figure 2.

Equation (7.25) permits us to define a criterion for the absence of interfacial mass-transport limitation, <u>viz.</u>,

$$\frac{H_A\ p_A(a) - [A]_a}{H_A\ p_A(a)} \leq \mathcal{E}_i << 1 \quad (7.26)$$

This criterion also sets an upper bound on the aqueous-phase reaction rate, in this case

$$\nu_A\ \bar{R}(a) \leq \mathcal{E}_i\ \frac{3\ \bar{v}\ \alpha}{4\ a\ \underset{\sim}{R}T} p_A(a)\ . \quad (7.27)$$

It is readily established that the bound (7.27) is equivalent to the intuitive supposition (7.21) for the absence of interfacial mass-transport limitation.

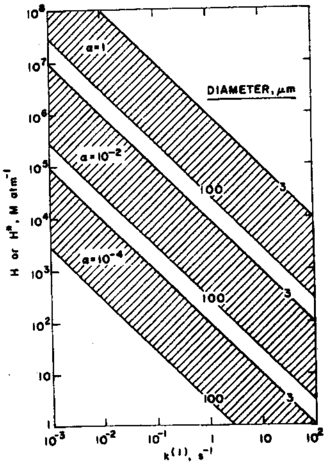

Figure 11. Interfacial mass-transport limitation. The several bands represent the onset (10%) of mass-transport limitation for the indicated values of accommodation coefficient α; the width of each band corresponds to the drop diameter range 3 to 100 μm. Mass-transport limitation is less than 10% if the point $(k^{(1)}, H)$ is below and to the left of the bound representing the applicable values of α and drop diameter. Evaluated for gas molecular weight = 30 g mol^{-1}.

The bound (7.27) may be expressed in terms of solubility and rate coefficients for various mechanisms just as was done in the examination of gas-phase mass-transport limitation. For first-order kinetics (eq. 5.5, $\nu = 1$) we obtain the bound

$$k^{(1)}\ H_A \leq \mathcal{E}_i\ \frac{3\ \bar{v}\ \alpha}{4\ a\ \underset{\sim}{R}T} \tag{7.28}$$

This inequality is illustrated in Figure 11, for $\mathcal{E}_i$ taken as 0.1. Here a range of bounds must be indicated reflecting both the pertinent range of drop size and the uncertainty in knowledge of α. It is seen by comparison to Figure 10 that interfacial mass-transport may be more or less controlling than gas-phase, depending largely upon the value of α. A similar treatment can be given for second-order kinetics yielding

$$k^{(2)} H_A{}^2 \leq \mathcal{E}_i\ \frac{3\ \bar{v}\ \alpha}{8\ a\ \underset{\sim}{R}T\ p_A}\ , \tag{7.29}$$

also exhibiting an inverse dependence on the partial pressure of the reacting gas. Such a situation has been treated by Schwartz (1984b).

Gas-Phase plus Interfacial.

We have observed that the description of both gas-phase and interfacial mass-transport is independent of the details of the aqueous-phase reaction mechanism. This observation suggests the utility of developing a single expression that combines both processes. Moreover, for the purpose of developing a formalism for treating mixed-phase kinetics at steady state, we shall find it useful to express the rate of these mass-transport processes by a single phenomenological "rate coefficient." We develop the expression for the mass-transport rate coefficient by analogy to the following model of a two-step reaction mechanism

$$X \underset{-1}{\overset{1}{\rightleftharpoons}} Y \qquad [1]$$

$$Y \xrightarrow{R_2} Z \qquad [2]$$

Reaction [1] is reversible with forward and reverse rate coefficient k_1 and k_{-1}; we note that the equilibrium constant for reaction [1] is $K_1 = k_1/k_{-1}$. Reaction (2) is irreversible, proceeding at steady state with rate R_2. The usual steady-state treatment for the concentration [Y] yields

$$\frac{[Y]}{K_1} = [X] - \frac{R_2}{k_1} \text{ .} \qquad (7.30)$$

We observe that an equation formally identical with (7.30) is obtained by combining equations (7.13) and (7.25) for gas-phase and interfacial mass transport, respectively, <u>viz.,</u>

$$\frac{[A(aq)]_a}{H_a} = p_A(\infty) - \underset{\sim}{R}T \left(\frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha}\right) \nu_A\ \bar{R}(a) \text{ .} \qquad (7.31)$$

We may thus make the following identification between elements of the reaction mechanism [1] - [2] and the mass-transport system:

$$X \ : \ A(g)_{r=\infty}$$

$$Y \ : \ A(aq)_{r=a}$$

$$[1] \ : \ A(g) \rightleftarrows A(aq)_{r=a}$$

$$R_1 \ : \ \frac{d_1[A(aq)]_a}{dt} = k_1\ p_A(\infty)$$

$$R_{-1} \ : \ \frac{d_{-1}[A(aq)]_a}{dt} = k_{-1}[A(aq)]_a$$

$$R_2 \ : \ \nu_A\ \bar{R}(a)$$

$$k_1 \ : \ \frac{1}{\underset{\sim}{R}T} \left(\frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha}\right)^{-1}$$

$$K_1 \ : \ H_A$$

$$k_{-1} \ : \ \frac{1}{H\underset{\sim}{R}T} \left(\frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha}\right)^{-1}$$

This identification is of considerable utility and exhibits as well a number of interesting features that we briefly discuss here. Before that, however, we introduce for convenience an additional definition, viz.,

$$k_{mt} = \left(\frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha}\right)^{-1} \ ; \qquad (7.32)$$

k_{mt} represents the rate coefficient for gas-phase plus interfacial mass transport. With this definition equation (7.31) becomes

$$\frac{[A(aq)]_a}{H_A} = p_A(\infty) - \frac{\nu_A\ \bar{R}(a)}{(\underset{\sim}{R}T)^{-1}\ k_{mt}} \ . \qquad (7.33)$$

A first observation concerns units, although to be sure the units of the several quantities are somewhat arbitrary, reflecting convention and definition. We note that we have chosen to express rates in aqueous-phase units, i.e., M(aq) s^{-1}. Thus for the phenomenological mass-transport reaction

$$[1] \qquad A(g)_{r=\infty} \rightleftharpoons A(aq)_{r=a}$$

the rate R_1 represents moles of reagent A entering the drop per liter of drop volume per second. Since, in keeping with the standard state convention we have adopted for gases, we wish to express the reagent gas activity as a partial pressure in units of atmospheres, the "rate coefficient" k_1 must have units M atm^{-1} s^{-1}. This falls out naturally in the identification

$$k_1 = \frac{1}{\underset{\sim}{R}T} \left(\frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha}\right)^{-1} \ . \qquad (7.34)$$

In defining k_{mt} according to (7.32) the choice was made to reflect the kinetics by k_{mt} (units: s^{-1}) and to effect the conversion of the concentration units by the factor $(RT)^{-1}$ (units: M atm^{-1}). It may be observed that

$$k_{mt}^{-1} = \frac{a^2}{3\ D_g} + \frac{4a}{3\ \bar{v}\alpha} \ , \qquad (7.35)$$

where the first term on the RHS is the characteristic time associated with gas-phase diffusion, $\tau_{d.g.}$, equation (7.10). We thus identify the second term as a characteristic time associated with interfacial mass transport,

$$\tau_i = \frac{4a}{3\ \bar{v}\alpha} . \qquad (7.36)$$

We therefore define a characteristic time associated with gaseous plus interfacial mass transport,

$$\tau_{mt} = k_{mt}^{-1} = \tau_{d.g.} + \tau_i \qquad (7.37)$$

i.e., the sum of the characteristic times of the two processes. Equations (7.35) and (7.37) reflect the usual combinatorial algebra associated with sequential mass-transport processes, i.e., of rate quantities "adding" like electrical conductances in series, or time quantities adding like resistances in series.

The dependence of the mass-transfer rate coefficient k_{mt} on accommodation coefficient and drop size is indicated in Figure 12. It is seen that for high values of α, k_{mt} approaches a constant value that represents diffusion-controlled uptake, whereas at small α k_{mt} decreases linearly with decreasing α, indicative of collision-controlled uptake. The <u>a</u> dependence at high α is quadratic, whereas at low α it is linear. We return to further consideration of k_{mt} in Section 8.

An important point to emphasize about the treatment that has been given thus far is that it is completely general with respect to the mechanism of the aqueous-phase reaction and with regard to whether or not the concentration profile of the reagent in the drop is spatially uniform. All that is assumed is that the aqueous-phase reaction is at steady state, proceeding with a spatially averaged rate $\bar{R}$. We would note, however, that in many cases of interest the aqueous-phase concentration profile is uniform, for which situation additional simplification obtains. Considerable simplification obtains as well in the case of a first-order aqueous-phase reaction (whether or not the aqueous concentration profile is uniform). For reaction [2] first-order in [Y], i.e.,

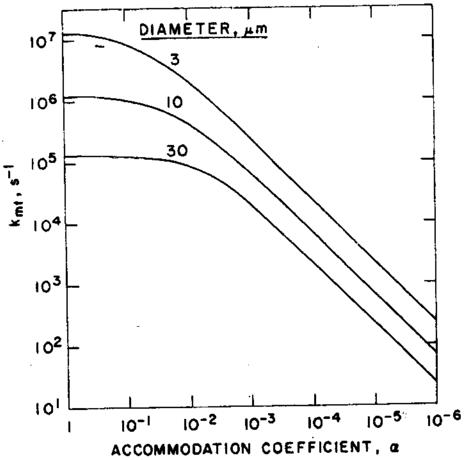

Figure 12. Dependence of the mass-transfer rate coefficient on accommodation coefficient and drop diameter. Note sense of log scale for α.

$R_2 = k_2[Y]$, we obtain from (7.30) the customary steady-state concentration

$$[Y] = \frac{k_1[X]}{k_{-1} + k_2} \; . \tag{7.38}$$

We make the further identification with the mass-transport system for first-order reaction with $\nu_A = 1$,

$k_2 \; : \; k_e{}^{(1)}$

$R_2 \; : \; k_e{}^{(1)}[A(aq)]_{r=a} \;\;;$

here $k_e{}^{(1)}$ is an effective first-order rate coefficient, which would be less than the intrinsic $k^{(1)}$ in the case of a non-uniform aqueous-phase concentration profile. We thus obtain

$$[A(aq)]_{r=a} = \frac{(\underset{\sim}{R}T)^{-1}\; k_{mt}\; p_A(\infty)}{(H_A\; \underset{\sim}{R}T)^{-1}\; k_{mt} + k_e{}^{(1)}} \; , \tag{7.39}$$

and in turn for the overall rate of reaction

$$R = \frac{k_e{}^{(1)}\; (\underset{\sim}{R}T)^{-1}\; k_{mt}\; p_A(\infty)}{(H_A\; \underset{\sim}{R}T)^{-1}\; k_{mt} + k_e{}^{(1)}} \; . \tag{7.40}$$

Equations (7.39) and (7.40) have two interesting limits. For $(H_A\; RT)^{-1}\; k_{mt} \gg k_e{}^{(1)}$, $[A(aq)] \approx H_A\; p_A(\infty)$, and $R \approx k_e{}^{(1)}\; H_A\; p_A(\infty)$, i.e., the phase-mixed limit, in which the aqueous-phase (at least at the interface, for non-uniform aqueous-phase profile) is in equilibrium with the reagent gas at the bulk partial pressure. At the other extreme, $(H_A\; \underset{\sim}{R}T)^{-1}\; k_{mt} \ll k_e{}^{(1)}$, $R \approx k_{mt}\; p_A/\underset{\sim}{R}T$, i.e., the reactive uptake is controlled completely by mass transport.

Some further comments are in order regarding equation (7.31) and in particular the term for mass-transport. We note that quite a few expressions of form similar to (7.32) have been advanced by various authors to describe mass-transport in the "Knudsen" regime, i.e., the regime intermediate between the continuum regime treated here and the free-molecular regime, in which the radius of the particle is much smaller than the gas mean free path (Wagner, 1982; Davis, 1983; Dahneke, 1983, and references therein). Of these expressions that due to Fuchs and Sutugin (1971), which was based on a numerical solution to a neutron scattering problem, is perhaps the most widely employed in consideration of mass-transport of minor solute species (e.g., Chameides and Davis, 1982). However, as emphasized by Davis (1983) all such expressions for mass-transport kinetics resulting from various simplified treatments are of necessity somewhat artificial because of inherent approximations. Undoubtedly the expression (7.32) would be subject to the same sort of criticism. However in support of the present treatment and the resulting expression for k_{mt} we would offer the following arguments:

1. Simplicity. Only continuum diffusion theory and the gas kinetic surface collision rate have been employed. No ad hoc assumptions have been made.

2. Comprehensiveness. The present model incorporates both reversible dissolution (according to Henry's law) and variable mass-accommodation coefficient.

3. Generality. The model is independent of the mechanism of aqueous-phase reaction and of any assumption regarding the aqueous-phase concentration profile.

4. Accuracy in the limits. The expression for the uptake rate approaches in the appropriate limit the correct value for the uptake rate in the continuum regime, in the free-molecular regime, and in the regime corresponding to Henry's law equilibrium between the concentration at surface of the drop and the bulk partial pressure.

To the above list one might also add the observation that comparison with the formula of Fuchs and Sutugin (1971) shows quite a close agreement over the entire range of mutual applicability, the maximum departure between the two expressions being 15%. These arguments certainly lend support to the present approach to evaluation of mass-transport kinetics for uptake and reaction of gases in aqueous droplets, and in particular to the mass-transport rate coefficient defined by equation (7.32).

Aqueous-Phase Diffusion and Reaction.

We now consider the problem of diffusion of a dissolved reagent from the surface of a drop toward the interior coupled with aqueous-phase reaction in the drop. We focus principally upon the steady-state treatment of this problem but briefly consider the time-dependent problem for the insights afforded. The objective of the analysis is to evaluate $\bar{R}_{ss}(a)$, the steady-state rate of reaction averaged over the volume of the drop, for the assumed chemical-kinetic rate law, as a function of the steady-state reagent concentration at the surface of the drop, $[A]_a$ (or $A_{ss}(a)$; Figure 2). This average rate may be compared with the rate evaluated under the assumption of a uniform reagent profile in the drop (at concentration $[A]_a$); the quotient of these two rates is a measure of the limitation imposed on the rate of reaction by the finite rate of aqueous-phase diffusion. We note further that evaluation of $\bar{R}_{ss}(a)$ as a function of $[A]_{r=a}$ permits evaluation of $[A]_{r=a}$ by (7.31) in terms of of the bulk partial pressure $p_A(\infty)$, thereby solving the entire problem of mass-transport (gas, aqueous, interfacial) coupled with aqueous-phase chemical reaction. The quotient of the average rate $\bar{R}_{ss}(a)$ to the rate evaluated for a uniform aqueous-phase concentration in Henry's law equilibrium with the bulk gas-phase concentration (A_∞ in Figure 2) is a measure of the overall mass-transport limitation.

We address the problem of coupled mass-transport and reaction by means of the partial differential equation in the time- and space-dependent aqueous-phase concentration A(r,t), analogous to (7.1) but inclusive of a term representing a reactive sink,

$$\frac{\delta A}{\delta t} - D_a \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta A}{\delta r}\right) + R(r,t) = 0 \ . \qquad (7.41)$$

Initially the concentration A is uniformly 0. At the time $t = 0$ the drop is exposed to a gas-phase concentration that establishes and maintains a constant surface concentration A(a). (We thereby assume that transients due to gas-phase and interfacial mass transport relax rapidly.) In the absence of the chemical sink term the concentration approaches a constant value equal to the surface concentration, with a time constant characteristic of aqueous-phase diffusion

$$\tau_{d.a.} = \frac{a^2}{\pi^2 D_a} \qquad (7.42)$$

(Crank, 1975, p. 92). For the reactive problem, at long time the system achieves a steady-state that is inherently characterized by a non-uniform concentration profile as the reagent is consumed by reaction in the interior of the drop. Introduction of the characteristic time associated with aqueous-phase diffusion allows us to anticipate the condition that must be satisfied in order that reaction not greatly deplete the aqueous-phase concentration from its surface value, viz.,

$$\tau_{d.a.} << \tau_r \qquad (7.43)$$

We return now to the reactive problem. At steady state $\delta A/\delta t = 0$ and the concentration profile is governed by the ordinary differential equation

$$D_a \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d\,A_{ss}(r)}{dt}) = R_{ss}(r) \tag{7.44}$$

Equations (7.41) and (7.44) are not in general analytically soluble. However in the case of a first-order rate law

$$R(r,t) = k^{(1)} A(r,t) \tag{7.45}$$

an analytical solution exists for both the time-independent and time-dependent problems. We therefore examine this system in some detail, not only to obtain a quantitative measure of the effect of mass-transport limitation but also for qualitative insight into other rate laws whose kinetics can be expressed in terms of an effective first order rate coefficient, as introduced in Section 5.

We first consider the steady-state solution to (7.44) with rate law (7.45), and return presently to the time-dependent solution. This solution is given (Schwartz and Freiberg, 1981) as

$$A_{ss}(r)=A(a) \frac{a}{r} \frac{\sinh\ (qr/a)}{\sinh\ q} \tag{7.45}$$

where we introduce the dimensionless diffuso-reactive parameter

$$q \equiv a(k^{(1)}/D_a)^{1/2} \ . \tag{7.46}$$

As we shall see, knowledge of the value of q characterizing a given physical system is fundamental to the understanding and description of the system.

In order to enable appreciation of the role of the parameter q upon the steady state concentration profiles within the drop, we show these profiles in Figure 13 for several values of q. It is seen that at low value of q, the steady state-reaction profile is nearly uniform. This reflects the rapidity of diffusion relative to reaction. However, for values of q of the order of unity and greater there is an appreciable depletion of A_{ss} towards the center of the drop, reflecting the inability of diffusion to restore the decrease in A_{ss} caused by chemical reaction. In other words, with increasing q there is decreasing penetration by A_{ss} from the surface of the drop into the interior. This effect is displayed also in Figure 14, in which the concentration at the center of the drop,

$$A_{ss}(0) = A(a) \frac{q}{\sinh\ q} \tag{7.47}$$

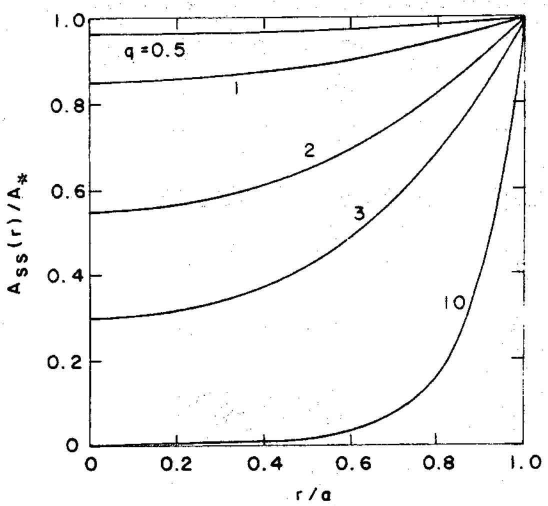

Figure 13. Steady-state radial concentration profiles of concentration of a reactant species A(r), relative to the concentration at the surface of the drop A_*, for a drop of radius a, for indicated values of the dimensionless parameter $q = a(k^{(1)}/D_a)^{1/2}$. In the notation of the present paper $A_* = A(a)$. From Schwartz and Freiberg (1981).

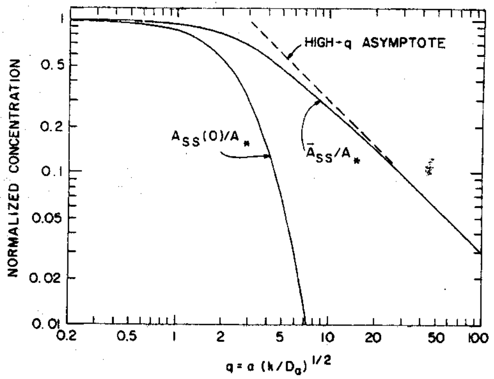

Figure 14. Average concentration of reactant species $\bar{A}$ and the concentration at the center of the drop A(0), relative to the concentration at the surface of the drop A_*, at steady state, as a function of q. From Schwartz and Freiberg (1981).

is given as a function of q.

More important than the dependence on q of the concentration at the center of the drop is the dependence on q of the average concentration $\bar{A}_{ss}$, since the rate of reaction averaged over the drop, $\bar{R} = k\bar{A}$, will at steady state be proportional to this average. $\bar{A}_{ss}$ is evaluated as

$$\bar{A}_{ss} = (4\pi a^3/3)^{-1} \int_0^a 4\pi r^2 A_{ss}(r)dr \ . \tag{7.48}$$

Integration of $A_{ss}(r)$ given in Eq. (7.45) yields the result

$$\bar{A}_{ss}/A(a) = 3 \left(\frac{\coth q}{q} - \frac{1}{q^2}\right) . \tag{7.49}$$

This steady-state average concentration is also shown in Figure 14 as a function of the parameter q. For $q \gtrsim 1$ the steady-state average concentration $\bar{A}_{ss}$ is seen to be significantly less than the equilibrium concentration A(a). The fall-off of $\bar{A}_{ss}$ with increasing q is slower than that of the concentration at the center, $A_{ss}(0)$. This slower fall-off reflects the large fraction of the volume of the drop that is "near" the surface. The dependence of $\bar{A}_{ss}$

and in turn $\bar{R}_{ss}(a)$ on $k^{(1)}$ and a, and the implications on the interpretation of laboratory kinetic data are discussed by Schwartz and Freiberg (1981) and Freiberg and Schwartz (1981). One particular feature to point out in the present context, however, is that the uptake remains first order in A(a). Hence it is useful to define an effective first-order rate coefficient, a function of drop radius <u>a</u>, that takes into account the non-uniform spatial-average concentration of A_{ss} in the drop, <u>viz.</u>,

$$k_e^{(1)}(a) \equiv 3k^{(1)} \left(\frac{\coth q}{q} - \frac{1}{q^2}\right) . \tag{7.50}$$

This effective first-order rate coefficient, which was suggested in the discussion above, is useful in consideration of reaction rates for distribution of drop sizes, as discussed in Section 8.

An important result that may be obtained from equation (7.49) is the value of q for which $\bar{A}_{ss}/A(a)$ commences to depart appreciably from unity. We observe that for low q (7.49) may be approximated as

$$\frac{\bar{A}_{ss}}{A(a)} \approx 1 - \frac{q^2}{15} + \frac{2q^4}{315} \ldots , \quad q \lesssim 1.5 . \tag{7.51}$$

Equation 7.51 permits a bound to be set on q, and in turn on k and that the fractional departure of the average concentration from that at the surface not exceed a specified value, <u>viz.</u>, for

$$1 - A_{ss}/A(a) \leq \mathcal{E}_a << 1 ,$$

$$k^{(1)} \leq 15 \, \mathcal{E}_a \frac{Da}{a^2} , \quad \mathcal{E}_a \leq 0.1 . \tag{7.52}$$

It is readily established that this bound is equivalent to the intuitive supposition (7.43) for the absence of aqueous-phase mass-transport limitation. The bound (7.52) is illustrated in Figure 10 for various values of drop diameter, for $\mathcal{E}_a$ arbitrarily taken as 0.1. For values of $k^{(1)}$ less than the bound indicated for the drop diameter aqueous-phase mass-transport limitation is minimized. The combined bounds represented by gas- and aqueous-phase mass-transport considerations restrict the values of ($k^{(1)}$, H_A) for situations free of mass-transport. Additionally, interfacial mass-transport limitation would also have to be addressed, Figure 11.

We note that the value of the Henry's law coefficient at the "knee" of the bound representing the onset of gas- and aqueous-phase mass-transport limitation is independent of drop radius, $\underline{a}$. This value of H is given by

$$H_{knee} = \frac{1}{5\ \underset{\sim}{RT}} \frac{D_g}{D_a} ,$$

for $\mathcal{E}_a = \mathcal{E}_g$. For $D_g = 10^4\ D_a$, $H_{knee} \approx 80$ M atm^{-1}. For values of $H < H_{knee}$, aqueous-phase mass transport is more controlling than gas-phase, and for $H > H_{knee}$, gas-phase mass transport is more controlling. Examples of the application of these relationships to measurement of mass-transport limitation for situations of interest in the ambient atmosphere have been given by Schwartz (1984a).

We now return briefly to the time-dependent problem, which has been treated in detail by Schwartz and Freiberg (1981) as well as other authors cited therein. An example of this time dependence is shown in Figure 15, which shows the concentration A(r,t) for the value q = 1.5, representative of a slight (~15%) steady-state mass-transport limitation. The several curves indicate the penetration of A into the interior of the drop and the eventual establishment of the steady-

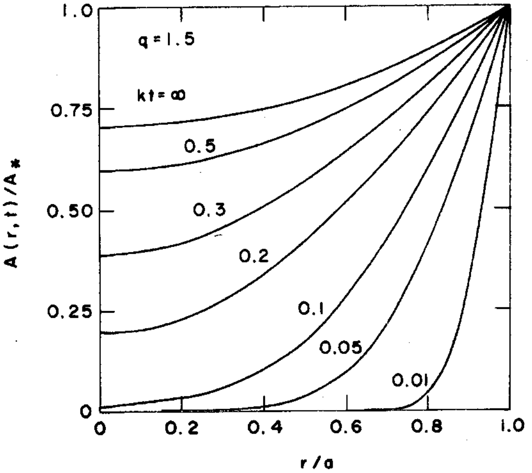

Figure 15. Values of the time- and space-dependent reagent concentration A(r,t) as a function of r for indicated values of $k^{(1)}t$, and for the diffuso - reactive parameter $q=a(k^{(1)}/D_a)^{1/2} = 1.5$. With increasing time the radial concentration function approaches the non-uniform steady-state profile; contrast Fig. 6.1 of Crank (1975) displaying profiles for diffusion in the absence of reaction, i.e., q = 0 in the present notation. From Schwartz and Freiberg (1981).

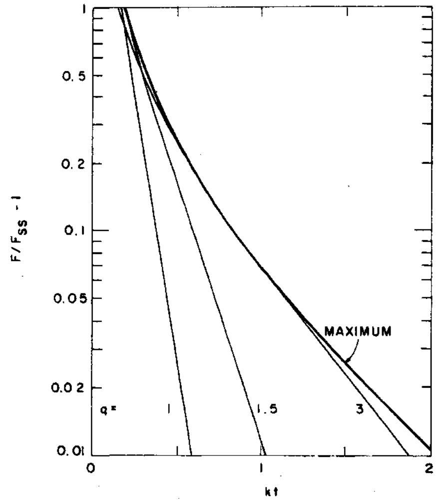

Figure 16. Time dependence of the relative difference between the flux into the drop at time t and the steady-state flux into the drop, for indicated values of q. Dark curve at right of figure represents the envelope of the several curves and constitutes an upper bound on the relative difference for all values of q. From Schwartz and Freiberg (1981).

state relationship. Perhaps more important is the present context in Figure 16, which shows the approach of the flux into the drop to the steady-state flux as a function of time for various values of q. This approach is seen to be rapid (relative to $\tau_r = k^{(1)-1}$) for all values of q, supporting the steady-state approach.

Aqueous-Phase Source.

For a reaction forming a product species C that diffuses within the aqueous phase and evolves into the gas phase the opposite situation obtains from that thus far treated, i.e., the normalized concentration profile on a plot such as Figure 2 decreases with increasing r. We briefly consider this problem to assess the magnitude of steady-state concentrations build-up as a function of reaction rate. As before gas-phase and interfacial results are independent of the details of R, but the aqueous-phase result depends on the radial distribution of R(r). For this discussion we take R to be constant.

Solution of the appropriate differential equations yields the following results:

$$\text{Aqueous:} \qquad \overline{[C]} - [C]_{r=a} = \frac{1}{15}\,\frac{a^2}{D_a}\,R$$

$$\text{Interfacial:} \qquad [C]_{r=a} - H_C p_C(a) = \frac{4\,H_C\,\underset{\sim}{R}T\,a}{3\,\bar{v}\alpha}\,R$$

$$\text{Gas phase:} \qquad p_C(a) - p_C(\infty) = \frac{\underset{\sim}{R}T\,a^2}{3\,D_g}\,R$$

$$\text{Total:} \qquad \overline{[C]} - H_C p_C(\infty) = \left[\frac{1}{15}\,\frac{a^2}{D_a} + H_C\,\underset{\sim}{R}T\left(\frac{4a}{3\,\bar{v}\alpha} + \frac{a^2}{3\,D_g}\right)\right] R$$

$$= \left[\frac{\pi^2}{15}\,\tau_{d.a.} + H_C\,\underset{\sim}{R}T\,(\tau_i + \tau_{d.g.})\right] R$$

These expressions permit evaluation of the magnitude of product build-up as a function of formation rate and pertinent mass-transport properties. Expression of each of the ΔC terms as a product of rate x characteristic time is particularly heuristic and therefore useful for acquiring insight into the system.

Summary.

In this section we have outlined a procedure for evaluation of mass-transport limitation to the reactive uptake of gases by aqueous droplets, treating gas-phase, interfacial, and aqueous-phase mass transport. The treatment was both heuristic, in terms of characteristic times (as summarized in Table 4), and quantitative, in terms of steady-state solutions to the pertinent differential equations. The treatment of gas-phase and interstitial mass-transport was general with respect to the aqueous-phase rate law, whereas the treatment of coupled aqueous-phase mass transport and reaction was restricted to a first-order rate law. Expressions were presented for the magnitude of departure from uniform concentration profile attributable to the several mass-transport processes; these are summarized in Table 5. Bounds representing the onset of mass-transport limitation were presented, as summarized also in Table 5. Finally the concentration profiles associated with aqueous-phase formation of product species were examined.

Table 4

Characteristic Times Pertinent to Reactions of Gases in Aqueous Droplets

Process	Characteristic Time	Definition	Equivalence
Reaction	τ_r	$[A]/\nu_A R$	
Aqueous-phase Diffusion	$\tau_{d.a.}$	$a^2/\pi^2 D_a$	
Gas-phase Diffusion	$\tau_{d.g.}$	$a^2/3D_g$	
Saturation by Gas-phase Diffusion	$\tau_{sat}^{(g)}$	$H\underset{\sim}{R}T \dfrac{a^2}{3\ D_g}$	$H\underset{\sim}{R}T\ \tau_{d.g.}$
Interfacial Mass Transport	τ_i	$\dfrac{4a}{3\ \bar{v}\alpha}$	
Saturation by Interfacial Mass Transport	$\tau_{sat}^{(i)}$	$H\underset{\sim}{R}T \dfrac{4a}{3\ \bar{v}\alpha}$	$H\underset{\sim}{R}T\ \tau_i$
Gas-phase + Interfacial Mass Transport	τ_{mt}	$\tau_{d.g.} + \tau_i$	

Table 5

Departure from Uniform Concentrations in Reactions of Gases in Aqueous Droplets

Phase	Magnitude of Departure	Uniformity Condition	
		Heuristic	Quantitative
Gas	$p(\infty) - p(a) = \frac{a^2 \underset{\sim}{R}T}{3 D_g} \nu R$	$\tau_{sat}^{(g)} \ll \tau_r$	$Hk^{(1)} \leq \varepsilon \frac{3 D_g}{\underset{\sim}{R}T a^2}$
Interfacial	$H_p - [A]_{r=a} = \frac{4a}{3 \bar{v}\alpha} H\underset{\sim}{R}T \nu R$	$\tau_{sat}^{(i)} \ll \tau_r$	$Hk^{(1)} \leq \varepsilon \frac{3 \bar{v}\alpha}{4a \underset{\sim}{R}T}$
Aqueous	$\overline{[A]}/[A]_{r=a} = 3 \left(\frac{\coth q}{q} - \frac{1}{q^2}\right)$	$\tau_{d.a.} \ll \tau_r$	$k^{(1)} \leq 15 \varepsilon \frac{D_a}{a^2}$

Aqueous phase departure and quantitative uniformity criteria are expressed for first-order rate law. Diffuso-reactive parameter $q = a(k^{(1)}/D_a)^{1/2}$.

$\varepsilon \leq 0.1$ represents maximum allowable fractional departure from uniformity condition.

8. GAS-AQUEOUS KINETICS IN CLOUDS

In this section we develop an approach to the description of reaction kinetics of gases in cloud droplets and the coupling of aqueous- and gas-phase kinetics. Such an approach in principle permits treatment of reactions in the two phases by means of a set of coupled ordinary differential equations.

Phase-mixed Limit.

Provided it can be established, by the methods outlined in Section 7, that the gas-aqueous reaction under examination is phase-mixed, then evaluation of aqueous-phase rates may proceed by the method outlined in Section 5, i.e, evaluation of aqueous-phase rates in terms of gas-phase partial pressures by Henry's law. This approach has been employed in our previous evaluations of the rates of aqueous-phase in-cloud reactions of nitrogen and sulfur oxides (Lee and Schwartz, 1981b; Schwartz, 1984a).

Monodisperse Cloud.

For non-phase mixed systems explicit consideration must be given to mass-transport kinetics. This treatment is heuristic for a monodisperse cloud, so we begin with this model.

Consider a monodisperse cloud, characterized by drop radius $\underline{a}$ and liquid-water volume fraction L. Consider a reaction mechanism

$$\mathrm{Q} \longrightarrow \mathrm{A(g)} \qquad [\mathrm{Q}]$$

$$\mathrm{A(g)} \longrightarrow \text{gaseous products} \qquad [\mathrm{S}]$$

$$\mathrm{A(g)} \rightleftharpoons \mathrm{A(aq)} \qquad [1]$$

$$\mathrm{A(aq)} \longrightarrow \text{products} \qquad [2]$$

Here [Q] and [S] represent gas-phase source and sink reactions of the reagent of concern A(g), having rates of q and s, respectively (atm s^{-1}). The following rate expression obtains for $[A]_a$ the aqueous-phase concentration of A, at the surface of the drop,

$$\frac{d[A]_a}{dt} = (\underset{\sim}{R}T)^{-1}\ k_{mt} p_A - (H_A \underset{\sim}{R}T)^{-1}\ k_{mt}[A]_a - \bar{R}_2, \qquad (8.1)$$

where we have used equation (7.34) for k_1. $\bar{R}_2$ represents the rate of reaction [2] averaged over the volume of the drop. The corresponding rate expression for p_A is

$$\frac{d\ p_A}{dt} = q - s - L\ k_{mt}\ p_A + \frac{L}{H_A} k_{mt}[A]_a\ , \qquad (8.2)$$

where we have used equation (5.3). Equations (8.1) and (8.2) form the basis for coupling of gas- and aqueous-phase chemical kinetics by the kinetics of inter-phase mass transport.

Before proceeding further it is useful to comment on the magnitude of the gas-aqueous exchange rate as represented by the term L k_{mt} p_A in equation (8.2). We have noted that the cloud liquid-water volume fraction L is of order 10^{-6}, and we observe from Figure 12 that k_{mt} is of order 10^{-3} s^{-1} ($\alpha \approx 10^{-5}$) to 10^{6} s^{-1} ($\alpha \geq 10^{-2}$). Thus the one-way fractional removal rate of a gas into the aqueous phase is of order 10^{-3} to 1 s^{-1}. This order-of-magnitude argument establishes potentially very high removal rates of reactive gases by aqueous-phase reactions in clouds. In this context we would note that Levine and Schwartz

(1982) have calculated aqueous-phase uptake rates of HNO_3 for representative cloud drop size spectra of 0.2 to 1 s^{-1}, under assumption of unit accommodation coefficient and irreversible dissolution. Such potentially high removal rates also suggest that aqueous-phase reactions would be competitive with gas-phase processes, including photolysis, provided aqueous-phase reactions are sufficiently fast. A possible example might be aqueous-phase reaction of N_2O_5 competing with photolysis of NO_3, and has recently been suggested by Heikes and Thompson (1983).

Polydisperse Cloud.

We now explicitly recognize that k_{mt} is a function of drop radius a and as a consequence $[A]_a$ and $\bar{R}_2$ are functions of a as well. Thus for each drop radius cut equation (8.1) becomes

$$\frac{d[A]_a(a)}{dt} = (\underset{\sim}{R}T)^{-1} k_{mt}(a)\, p_A - (H_A\, \underset{\sim}{R}T)^{-1} k_{mt}(a)[A]_a(a) - \bar{R}_2(a) \quad . \qquad (8.3)$$

In turn for the contribution to the mass-transport kinetics of A(g) due to cloud drops of size a we obtain

$$\frac{d_{mt}\, p_A}{dt} = - p_A\, k_{mt}(a)\, \delta L(a) + \frac{1}{H_A}\, k_{mt}(a)\, [A]_a(a)\, \delta L(a) \quad , \qquad (8.4)$$

where $\delta L(a)$ is the partial liquid-water volume fraction in the size cut corresponding to a,

$$\delta L = (\frac{4}{3}\pi\ a^3)\ (\frac{dN}{da})\ \delta a,$$

see Figures 3 and 4. The total mass transport rate expression is obtained by integration over the partial volume spectrum of the cloud,

$$\frac{d_{mt} p_A}{dt} = - p_A \int k_{mt}(a)\ dL + \frac{1}{H_A} \int k_{mt}(a)\ [A]_a\ dL \quad , \qquad (8.5)$$

Equations 8.3 and 8.5 provide the basis for a set of coupled differential equations in the gas-phase and aqueous species. In practice, application of these equations to evaluation of rates for real or model systems will require either use of a model drop-size distribution of summation over size cuts as indicated in Section 3.

For aqueous-phase reaction by first-order reaction it is useful to treat the aqueous-phase concentration by the steady-state approximation. We note that for a first-order reaction $R_2(a) = k_e^{(1)}(a)\ (A)_a$, where $k_e^{(1)}$ is the effective first-order rate coefficient defined relative to the surface concentration (eq. 7.50).

Setting $\frac{d[A]_a(a)}{dt} = 0$ in equation (8.3) we obtain

$$[A]_a(a) = (\underset{\sim}{R}T)^{-1}\ p_A \frac{k_{mt}(a)}{(H_A\underset{\sim}{R}T)^{-1}\ k_{mt}(a) + k_e^{(1)}(a)}\ , \qquad (8.6)$$

and in turn

$$\bar{R}_2(a) = (\underset{\sim}{R}T)^{-1}\ p_A \frac{k_e^{(1)}(a)\ k_{mt}(a)}{(H_A\underset{\sim}{R}T)^{-1}\ k_{mt}(a) + k_e^{(1)}(a)}\ . \qquad (8.7)$$

Equation (8.7) embodies the dependence of the rate of aqueous-phase reaction on the size of the drop and provides a basis for anticipating that gas-aqueous reactions will proceed at a faster rate in smaller drops, expressed on a molar basis. In turn one would anticipate that the concentrations of non-volatile product species will increase in smaller drops at faster rates than in larger drops, and that this higher concentration might be measurable by means of a fractionating cloudwater collector. On the other hand, the increased solute concentration of the smaller drops might lead to an enhanced accretion rate of water vapor, at the expense of the supersaturation or even of the larger drops. This process would result in a leveling of the solute concentration distribution and a narrowing of the drop-size distribution.

9. SUMMARY

A formalism exists that permits description of the kinetics of mass-transport processes in the uptake of gases by aqueous droplets and aqueous-phase chemical reaction for droplets in the size range pertinent to liquid-water clouds. These mass-transport processes are gas-phase diffusion, gas-kinetic collision at the interface, and aqueous-phase diffusion coupled with chemical reaction. Criteria are presented whereby it may be readily discerned, as a function of drop size, reaction rate coefficient, and mass-accommodation coefficient whether a system under examination may be treated as phase mixed or whether more detailed treatment of mass-transport limitation is required, and expressions are presented by which mass-transport limitation can be evaluated.

One finding that emerges from the treatment of mass-transport kinetics is the dominance of interfacial mass-transport limitations for values of the mass-accommodation coefficient less than 10^{-2}. Unfortunately, little information is available pertinent to this quantity for solute gases with liquid water. The potential importance of interfacial mass-transport limitation to the rate of gas-aqueous reactions in clouds indicates the need for laboratory studies directed to determination of this quantity.

ACKNOWLEDGMENT

This work was supported in part by the Electric Power Research Institute (Project RP2023-1) and was performed under the auspices of the Department of Energy under Contract No. DE-AC02-76CH00016.

PRINCIPAL NOMENCLATURE

a	Drop radius, cm.
A,[A]	Aqueous-phase concentration of species A, M.
D	Diffusion coefficient, $cm^2\ s^{-1}$.
F	Flux, mol $cm^{-2}\ s^{-1}$.
g	Gravitational constant, $cm^2\ s^{-1}$.
G	Gas-phase concentration, M.
H_X	Henry's law coefficient of species X, M atm^{-1}.
$k^{(m)}$	Reaction rate coefficient for m^{th} order reaction, $M^{-(m-1)}\ s^{-1}$.
k_n	Reaction rate coefficient of reaction [n].
k_{mt}	Rate coefficient for gas-phase plus interfacial mass transport, s^{-1}.
L	Liquid water volume fraction (of cloud).
N	Drop number density (of cloud), cm^{-3}.
p_X	Partial pressure of species X, atm.
q	Diffuso-reactive parameter, $a(k^{(1)}/D_a)^{1/2}$
r	Radius variable, cm.
R_n	Rate of reaction [n], M s^{-1}.
$\underset{\sim}{R}$	Universal gas constant, $atm^{-1}\ M^{-1}\ K^{-1}$ except where indicated.
T	Absolute temperature, K.
$\bar{v}$	Mean molecular speed, cm s^{-1}.
α	Mass accommodation coefficient.
ε	Maximum allowable departure from uniformity condition.
η	Dynamic viscosity, g $cm^{-1}\ s^{-1}$.
νX	Stoichiometric coefficient of species X in reaction.
ρX	Fractional rate of reaction of gaseous species X, s^{-1}.
σ	Interfacial collision flux, mol $cm^{-2}\ s^{-1}$.
τ	Characteristic time, s (see Table 4).

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