FACTORS GOVERNING DRY DEPOSITION OF GASES TO SURFACE WATER

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ABSTRACT

Rates of dry deposition of gases to surface water vary by orders of magnitude depending on the concentration of the gas in the surface water and on the solubility and aqueous-phase reaction kinetics of the depositing gas. For non-reactive gases the key property is the Henry's law solubility. For reactive gases the deposition flux can be quantitatively related to the chemical reaction rate for known mass-transport parameters and solubility and kinetic coefficients of the depositing gas. Interfacial resistance to mass transport does not seem to be significant based upon recent laboratory measurements of mass-accommodation coefficients. Readily applicable criteria to identify controlling processes are presented and applied to examination of SO_2 (gas-phase mass-transport control), CO_2 (liquid-phase mass-transport control), and formaldehyde and O_3 (liquid-phase chemical-kinetic control) as examples.

1. INTRODUCTION

Dry deposition of trace constituent atmospheric gases to surface water represents an important process by which these substances are removed from the atmosphere and taken up by surface water. Rates of dry deposition are commonly expressed as deposition velocities, the ratio of the deposition flux of the gas to its atmospheric concentration. The magnitudes of deposition velocities can be as great as a few centimeters a second, limited by the rate of transfer of the gas to the surface by atmospheric transport processes. Such a rate can make dry deposition a major sink process. For the height of the mixed layer of the atmosphere taken as 1 km, a deposition velocity of 1 cm s^{-1} results in a lifetime of 10^5 s or about 1 day. However deposition velocities can be much less–consider the deposition velocities of gases such as ozone, methane, or argon. It is thus of interest to examine the processes that control this dry deposition. These processes include mass transport in the atmosphere and in the water, reversible dissolution at the interface, and chemical reaction in solution.

This article examines the factors controlling dry deposition of gases to surface water, especially chemical factors. The examination employs a modification of the two-film theory that explicitly treats enhancement of the rate of gas-liquid

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exchange by chemical reaction that goes back at least to Danckwerts and Kennedy (1954). Depending on the relative rates of the several component steps one or another process may be controlling, and these may be readily identified. This identification frequently leads to a simplification of the expression describing dry deposition and provides insight into the relation between the deposition velocity and the rate and nature of the processes responsible for this deposition.

A key point that should be emphasized is that the dry deposition flux is a net flux, the difference between a downward flux of the gas from the air into the water and an upward flux from the water into the air. In many cases of interest the latter is negligible, so that the net deposition flux is equal to the gross downward flux. In this case the deposition velocity is controlled entirely by the rate of atmospheric mass-transport processes and is only weakly dependent on the identity of the gaseous species, varying perhaps as much as the diffusion coefficient. If the deposition velocity is appreciably less, then the air-water transfer must be viewed as reversible, the net flux representing the difference between two larger, opposing gross fluxes. This requires that the concentration of the dissolved gas must be appreciable compared to the equilibrium (Henry's law) concentration at the surface, although not necessarily in the bulk. Only by recognizing this can we make much headway in understanding the processes that control this deposition.

2. THEORY

The exchange flux of a gaseous species between the gas and aqueous phases may be described phenomenologically (e.g., Danckwerts, 1970) as the product of an overall mass-transfer coefficient K_G times the difference between the gas-phase concentration G and the aqueous-phase concentration A divided by the dimensionless Henry's law coefficient H describing the equilibrium solubility of the gas in the aqueous medium [mol/cm^3 (aq) ÷ mol/cm^3 (g)]:

$$F = K_G (G - A/H). \tag{1}$$

For application to atmosphere-surface water exchange the choice of the reference height and reference depth at which to measure G and A is rather arbitrary provided that it is not too close to the surface–a few meters or more in the atmosphere; a few decimeters in the water. The reason for this is that at such distances the rate of mass transport, by eddy or turbulent diffusion processes, is sufficiently great that there is not much gradient in concentration. The reader is cautioned that numerous definitions for Henry's law coefficients, having different units and even different senses, have been and continue to be used by different investigators.

It is evident from (1) that in order for there to be a net flux the aqueous-phase concentration A must not be in equilibrium with the gas-phase concentration G, i.e., $A \neq HG$, and more specifically that for there to be a net downward (deposition) flux, A must be less than HG. The lack of equilibrium leading to deposition may be due to aqueous-phase chemical reaction depleting the concentration the dissolved gas or, alternatively, simply to the fact that the water is undersaturated relative to the atmospheric concentration of the gas, for example because of transfer from the mixed layer of the ocean to the deep ocean.

All of the physics of the mass-transfer process is embodied in the mass-transfer coefficient K_G. This quantity, like the deposition velocity, has dimension of length/time, or velocity. If the aqueous-phase concentration of the depositing substance A is 0 (more precisely, if $A << HG$), then $F = K_G G$; that is, the deposition velocity is equal to K_G. However, the condition $A << HG$ does not necessarily imply that the deposition flux is equal to its maximum possible value, as governed by atmospheric mass transport only, since there may be a return flux (surface water to atmosphere) resulting from a near-surface aqueous-phase concentration that is substantial compared to HG even when $A << HG$.

The choice of the gas-phase concentration, rather than the aqueous-phase concentration, as that to which to refer the flux is arbitrary, reflecting our gas-phase orientation. The flux might entirely equivalently be referred to the aqueous-phase concentration, viz.,

$$F = K_L (HG - A); \tag{2}$$

it is seen that $K_L = K_G / H$.

Considerable progress is made in understanding and describing the overall mass-transfer process by considering it to be a sequence of processes, from the bulk gas phase to the interface, across the interface, and from the interface to the bulk aqueous phase. These fluxes are described, respectively, as:

$$F = k_G (G - G_i) \tag{3}$$

$$F = (\frac{1}{4})\bar{v}\alpha(G_i - A_i / H) \tag{4}$$

$$F = \beta k_L (A_i - A) \tag{5}$$

Here the subscript i denotes the concentration immediately adjacent to the interface. The gas-phase and liquid-phase mass-transfer coefficients k_G and k_L describe physical mass transfer–turbulent diffusion plus molecular diffusion through the laminar boundary layer immediately adjacent to the interface; the magnitudes of these coefficients depend on the degree of physical agitation characterizing the system, as influenced principally by wind stress (Hicks and Liss, 1976; Liss and Merlivat, 1986). The coefficient β, to be discussed presently, represents enhancement of the aqueous-phase mass-transfer flux due to removal of the material by chemical reaction; when there is no enhancement $\beta = 1$. Transport of material across the interface, which can be achieved only by collisions of molecules with the interface, occurs at the gas kinetic collision rate $(1/4)\bar{v}G$, multiplied by a mass-accommodation coefficient α, the probability that a collision will result in interfacial mass transfer. Here $\bar{v}$ is the mean molecular speed of the molecule.

Under steady-state conditions the flux is constant and equal in both media and across the interface. By equating the several expressions for the flux one obtains the overall mass-transfer coefficient as the inverse sum of the mass-transfer coefficients in the two media and at the interface:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{(\frac{1}{4})\bar{v}\alpha} + \frac{1}{Hk_L\beta}. \tag{6}$$

The several terms in (6) add like electrical resistances in series, and to extend the analogy the inverses of these quantities might be considered conductances. Once the values of these several terms are known it is frequently possible to identify a single term that greatly exceeds the others. Such a situation indicates that the mass transfer is completely controlled in that phase (the "voltage drop" is completely across that "resistor") and that attention can thus be focused on that phase. As we shall see, magnitudes of mass-accommodation coefficients appear to be sufficiently great that interfacial resistance is negligible. A possible exception to this generalization might arise for surfaces covered by surfactant films, but in the natural environment such films do not seem to persist (Liss, 1983).

In the absence of any aqueous-phase chemical reaction of the dissolved gas that would enhance the rate of uptake the enhancement coefficient β is equal to unity. This corresponds to the two-film expression commonly employed in evaluating air-sea fluxes of nonreactive gases (e.g., Liss and Slater, 1974). Assuming that the interfacial resistance is negligible, then there is a critical solubility $H_{\mathrm{crit}} \equiv k_G/k_L$ for which the gas- and liquid-phase resistances are equal. For $H << H_{\mathrm{crit}}$ liquid-phase mass transport is controlling and the uptake rate is linearly dependent on H. For $H >> H_{\mathrm{crit}}$ gas-phase mass transport is controlling and the uptake rate is independent of H. For reactive gases the effect of the chemical removal process is exhibited in the enhancement coefficient β, and it is βH that is to be compared to H_{crit}.

Te examine reactive enhancement of uptake it is necessary to model the concurrent mass-transfer and reactive processes, and a number of models have been introduced over the years, largely in the chemical engineering literature. The most familiar such model is the so-called diffusive-film model, which posits an unstirred laminar film at the interface having thickness D_{aq}/k_L, where D_{aq} is the molecular diffusion coefficient of the dissolved gas. The reactive gas must diffuse through this film to the bulk convectively mixed liquid. Reaction occurs in the film and/or in the bulk liquid depending on the relative rates of reaction and mass transport. Although criticized as unrealistic, this model has received widespread application in the geochemical literature. Alternative models posit systematic or stochastic transport of stagnant, near-surface parcels of liquid into the bulk, again with reaction occurring to greater or lesser extent in these unstirred parcels depending on the relative rates of reaction and mass transport. In all cases the liquid-phase mass transport is characterized by the single parameter k_L as well as by D_{aq}.

Rates of reactive uptake for the three models were examined and compared by Danckwerts and Kennedy (1954). For the diffusive film model the expression for β for a reversible first-order reaction of the dissolved gas can be written as:

$$\beta = \frac{\eta}{1 + (\eta - 1)\left(\frac{\tanh \kappa^{1/2}}{\kappa^{1/2}}\right)} \tag{7}$$

Here η is the ratio at equilibrium of the total concentration of dissolved material to the concentration given by Henry's law dissolution alone, and κ is a dimensionless rate coefficient for reaction,

$$\kappa = \frac{k^{(1)}}{k_{\mathrm{L}}^{2} / D_{\mathrm{aq}}} \cdot \frac{\eta}{\eta - 1}. \tag{8}$$

where $k^{(1)}$ is the effective first-order rate coefficient for aqueous-phase reaction of the dissolved gas.

A word should be said about the factors $\eta/(\eta-1)$ and $k_{\mathrm{L}}^{2}/D_{\mathrm{aq}}$ employed in the definition of κ. At $\eta >> 1$, which corresponds to large equilibrium enhancement of the solubility and which is almost always the situation of interest, $\eta/(\eta-1) \approx 1$ and can thus be neglected in evaluation of κ. At low values of η (recall that $\eta \geq 1$) the factor $\eta/(\eta-1)$ gives rise to substantial enhancement of κ essentially because the reaction doesn't need to proceed very far to reach equilibrium. The quantity $k_{\mathrm{crit}} \equiv k_{\mathrm{L}}^{2}/D_{\mathrm{aq}}$ has dimension of inverse time; comparison of $k^{(1)}$ with k_{crit} permits the importance of reactive enhancement to the rate of uptake to be immediately assessed.

Despite the somewhat different and more realistic assumptions of the surface renewal models these models were found to yield expressions for β that differ from (7) by no more than a few percent (Danckwerts and Kennedy, 1954). These models have gained substantial support in laboratory studies (e.g., Danckwerts, 1970). Expressions for the kinetic enhancement equivalent to (7) were later obtained in the context of atmosphere-surface water exchange by Bolin (1961) and by Hoover and Berkshire (1969) and are sometimes is associated with those investigators.

Although all that remains to evaluate β (and ultimately K_{G}) is knowledge of the pertinent parameters, it is worthwhile to examine the dependence of the enhancement of uptake on the equilibrium constant and reaction rate constant, especially as many people do not immediately relate to the hyperbolic tangent. One should be assured, however, that this is a very benign function. At low values of the argument (≤ 0.5), i.e., for low reaction rate coefficients, the function closely approximates the argument itself, so that $\tanh \kappa^{1/2} / \kappa^{1/2}$ approaches unity and in turn β approaches unity. Thus approximately (within 10%)

$$\beta \approx 1 \qquad \text{for } \kappa \leq 0.3. \tag{7a}$$

In this limiting situation there is essentially no enhancement of the rate of uptake over that given by physical dissolution alone. For somewhat greater values of κ, where the enhancement becomes appreciable, β is approximated by series expansion of the tanh function (again within 10%) as:

$$\beta \approx 1 + \frac{1}{3}\frac{\eta - 1}{\eta}\kappa = 1 + \frac{1}{3}\frac{k^{(1)}}{k_{\mathrm{L}}^{2}/D_{\mathrm{aq}}} \qquad \text{for } \kappa \leq 2.1. \tag{7b}$$

At the other extreme, for values of the argument of tanh greater than about 1.5 (i.e., at high reaction rates), tanh approaches unity, and to good approximation

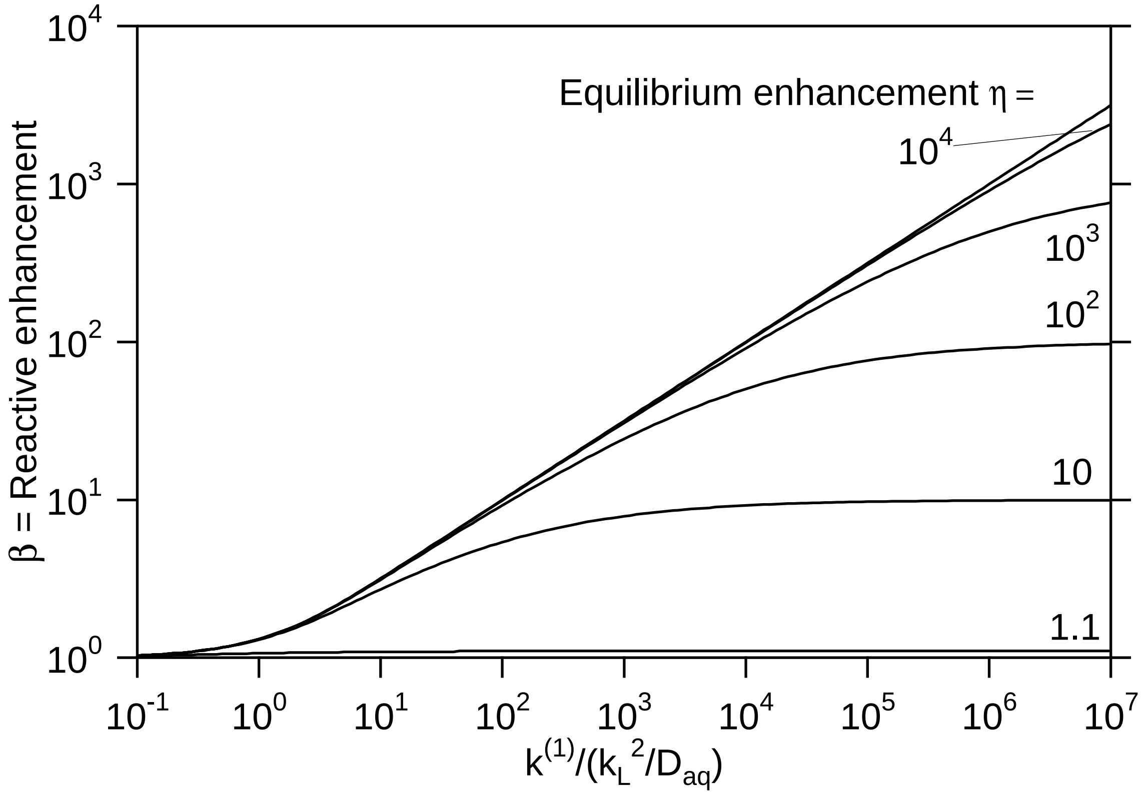

FIGURE 1. Dependence of the kinetic enhancement factor β of the aqueous-phase mass-transfer coefficient k_L as a function of the effective first-order rate coefficient for reaction $k^{(1)}$, normalized to k_L^2 / D_{aq}, where D_{aq} is the aqueous-phase molecular diffusion coefficient, for indicated values of the equilibrium solubility enhancement factor η.

$$\beta \approx \frac{\eta}{1+\dfrac{\eta-1}{\kappa^{1/2}}} \equiv \frac{\kappa^{1/2}}{1+\dfrac{\kappa^{1/2}-1}{\eta}} \quad \text{for } \kappa \geq 2.4. \tag{7c}$$

For values of κ such that $(\kappa^{1/2}-1) << \eta$ this expression simplifies to

$$\beta \approx \kappa^{1/2} \qquad \text{for } 2.4 \leq \kappa \leq (1+0.1\eta)^2. \tag{7d}$$

Finally, if $\kappa^{1/2}$ is sufficiently great, the second term in the denominator of (7) predominates and

$$\beta \approx \kappa^{1/2} \qquad \text{for } 2.4 \leq \kappa \leq (1+0.1\eta)^2. \tag{7e}$$

In this limit the rate of uptake is equal to that for a non-reactive gas whose solubility is enhanced, due to instantaneous chemical equilibrium, by the factor η. This limit justifies the use of an effective Henry's law coefficient $H^* = \eta H$ in eq (1) for rapidly established equilibria and specifies the range of applicability of this treatment.

The dependence of β on the effective first order rate coefficient for reaction $k^{(1)}$ is illustrated in Figure 1 for a range of values of η. The plateauing of β for large values of $k^{(1)}$ and intermediate values of η corresponds to the limit (7e). The linear region of the graphs (slope = 1/2 on the logarithmic plot) corresponds to the limit (7d). This is equivalent to the well known (Danckwerts, 1970) expression for diffusion controlled reaction for $\eta >> 1$,

$$\beta k_{\mathrm{L}} \approx (k^{(1)} D_{\mathrm{aq}})^{1/2} \qquad \text{for } 2.4 \leq \ \kappa \leq (1+0.1\eta)^2 . \tag{9}$$

We return later to consideration of reactive enhancement of uptake for specific examples of atmospheric interest, referring to the several above regimes by the letters following the equation numbers.

3. MASS-TRANSPORT PARAMETERS

In order to apply the above expressions to evaluate deposition fluxes in the atmosphere it is necessary to know values of the pertinent parameters particularly k_{G} and k_{L} . Hicks and Liss (1976) show that k_{G} is roughly 0.13% of the wind speed, for a reference height of 10 m; the exact proportionality coefficient depends somewhat on the reference height and on the atmospheric stability. Thus for typical wind speeds of 3 to 15 m s^{-1}, values of k_{G} range from 0.4 to 2 cm s^{-1}. An expression for k_{L} given by Liss and Merlivat (1986), which exhibits three linear regions of dependence on wind speed (increasing slope with increasing wind speed), has gained substantial support (e.g., Watson et al, 1991). That expression gives $k_{\mathrm{L}} = 1.4 \times 10^{-4}$, 1.3×10^{-3}, and 1.1×10^{-2} cm s^{-1} for wind speeds of 3, 5, and 10 m s^{-1}; the actual values depend somewhat on the identity of the transported gas and on temperature. We take these values as representative of the range that must be considered for the present purpose of identifying factors governing dry deposition of gases to surface waters. However it must be stressed that although these values are representative, the problem of specifying the precise values pertinent to a given environmental situation is by no means solved.

Figure 2 shows the overall mass-transfer coefficient K_{G} in the absence of reactive enhancement as a function of solubility for representative values of k_{G} and k_{L}. This is not a very interesting graph *per se*. What makes the figure interesting is the display of Henry's law and effective Henry's law coefficients along the abscissa. The points marked by • represent the equilibrium solubility after the reaction (acid-base dissociation, pH dependent, or aldehyde hydrolysis) has gone to completion; the ratio to the physical solubility (indicated by |) gives the equilibrium enhancement factor η. The thrust of the figure is that without reactive enhancement there are few gases that are sufficiently soluble in water without further reaction that for representative values of k_{G} and k_{L} their deposition velocity is controlled by atmospheric mass transport. This figure should serve to demonstrate the importance of reactive enhancement to k_{L}.

A further feature of the figure is the device at the upper right, which displays the interfacial conductance, evaluated as $(1/4)\bar{v}\alpha$, for indicated values of the mass-accommodation coefficient α. Here the mean molecular speed, which depends on molecular weight, has been taken as 4×10^4 cm s^{-1}. Interfacial conductance, should be taken into consideration if it is comparable to K_{G} evaluated with only the gas- and liquid-phase resistances. Interfacial resistance is not limiting for values of $\alpha \gtrsim 10^{-4}$ but , depending on the value of K_{G} evaluated with only the gas- and liquid-phase resistances, may become limiting for lower values of α.

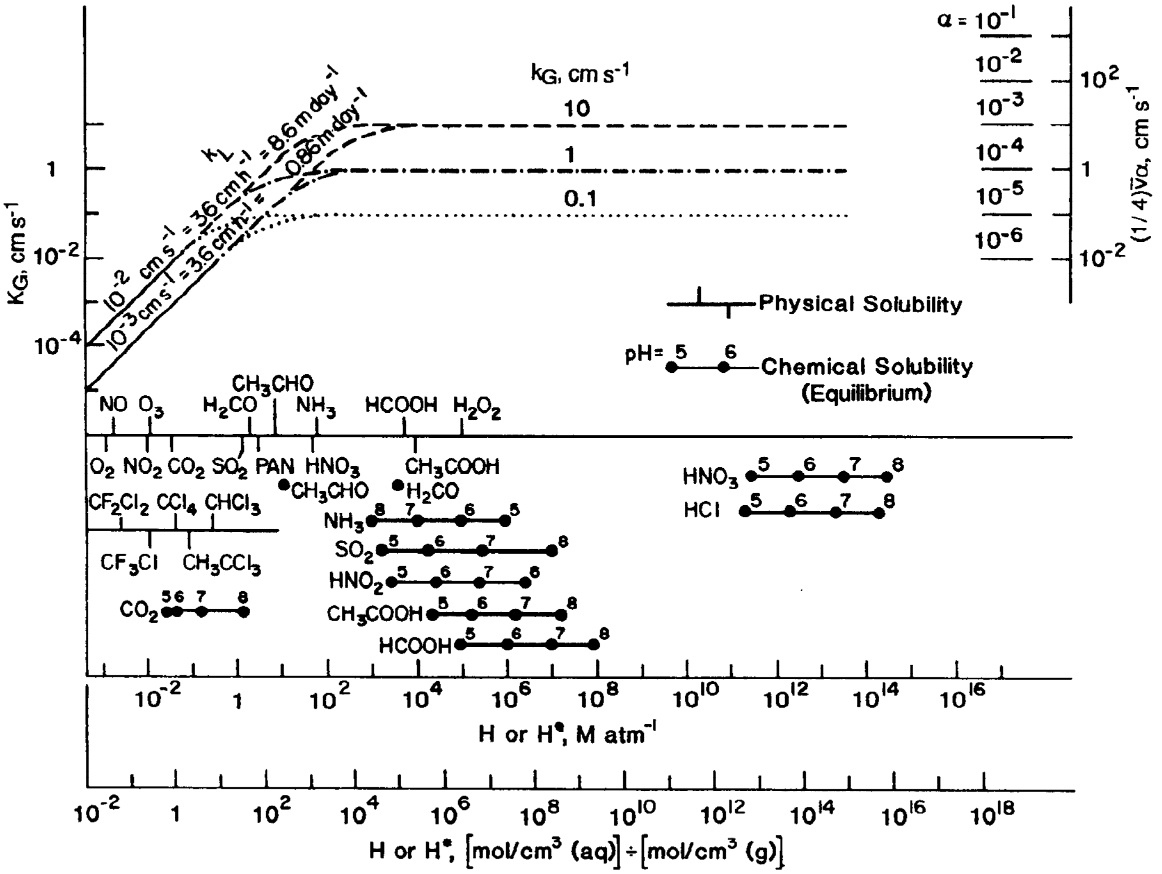

FIGURE 2. Overall mass-transfer coefficient K_G (in the absence of interfacial mass-transport limitation) for non-reactive gases ($\beta = 1$) as a function of solubility for values of k_G and k_L indicated on the asymptotes of the curves. Scale at right permits comparison of interfacial and overall conductance for indicated values of the mass-accommodation coefficient α. Also shown are Henry's law coefficients H (I) and effective Henry's law coefficients H^* (•) of a number of atmospheric gases; the intermediate abscissa scale gives H and H^* in units of molar per atmosphere favored by chemists. Modified from Slinn (1984).

Substantial advances have been made in recent years in determining mass-accommodation coefficients of gases at the air-water interface. Although early work (Baldwin and Golden, 1979) had been interpreted as showing that mass-accommodation coefficients of common atmospheric gases were as low as 10^{-6}, recent studies have shown that for many gases mass-accommodation coefficients are within an order of magnitude of unity (Worsnop et al., 1989; Van Doren et al., 1990; Jayne et al., 1991), although for some gases they are markedly lower: 5×10^{-4} for O_3 and 6×10^{-4} for NO_2 (Tang and Lee, 1987; Lee and Tang, 1988). In principle therefore interfacial mass-transport might appear to inhibit deposition of the latter two gases. However, because of their low solubilities, interfacial mass-transport limitation would decrease the overall deposition flux of these gases only for impossibly great reactive enhancement of solubility. It therefore seems that interfacial mass-transport limitation to dry deposition of gases to surface water may be disregarded. To this conclusion one might add a caveat regarding inhibition of mass transport by surfactant films, although as noted above this does not seem to be a frequent phenomenon.

4. EXAMPLES

A few illustrative examples are sketched here. For additional discussion with numerous examples see Thompson and Zafiriou (1983), and for an extended discussion of NO_2 see Lee and Schwartz (1981). For the present examples we choose the following representative values of the pertinent mass-transport parameters: k_G, 1 cm s^{-1}; k_L 3×10^{-3} cm s^{-1}; D_{aq}, 1×10^{-5} cm^2 s^{-1}. For these parameters $H_{crit} = 300$ and $k_{crit} = 1$ s^{-1}.

4.1 Sulfur Dioxide

SO_2 is a slightly soluble ($H \approx 30$), moderately acidic (pK = 1.7) gas, which dissociates rapidly ($k^{(1)} = 4 \times 10^6$ s^{-1}; Eigen et al., 1964) to yield $HSO_3^- + H^+$; the second dissociation, to $SO_3^=$, has a pK of 7.2. Oxidation of sulfite ion to sulfate on a time scale of minutes to hours serves as a permanent sink of S(IV) precluding its build up to substantial concentration in bulk surface water. The equilibrium enhancement $\eta \approx 2 \times 10^4$ for surface water pH of 6 and is even greater for higher pH, yielding $H^* \approx 6 \times 10^5$ for pH 6; *cf*. Figure 2. However for $k_{crit} = 1$ s^{-1}, $\kappa \approx 4 \times 10^6$, and since this is well less than η^2, the mass-transport situation is squarely in the diffusion controlled reaction regime (d), yielding $\beta = \kappa^{1/2} \approx 2000$, and not in the equilibrium regime (e) as is frequently assumed. Despite this, since $\beta H >> H_{crit}$, the uptake remains gas-phase controlled, the point is moot.

4.2 Carbon Dioxide

CO_2 is much less soluble than SO_2 ($H \approx 1$) and much less acidic (pK = 6.4). It dissociates slowly ($k^{(1)} = 4 \times 10^{-2}$ s^{-1}; Eigen et al., 1964) to yield $HCO_3^- + H^+$; the second dissociation, to $CO_3^=$, has pK of 10.3. Also in contrast to SO_2, dissolved inorganic carbon, C(IV) is not chemically depleted in surface water but is produced, by photosynthesis, as well as removed by chemical and biological processes, so the driving force for mass transport may be upwards or downwards as a function of time and location. The low value of $k^{(1)}$, and the correspondingly low value of κ (≈ 0.04), place CO_2 squarely in regime (a)–no enhancement due to reaction–and the low solubility makes this exchange controlled entirely by liquid-phase mass transport.

4.3 Formaldehyde

H_2CO ($H \approx 50$; Blair and Ledbury, 1925) undergoes reversible hydration in water ($k^{(1)} \approx 10$ s^{-1}; Bell and Evans, 1966) to form $H_2C(OH)_2$, with $\eta \approx 2000$ (Bell and Evans, 1966); *cf*. Figure 2. For the above representative mass-transport properties $\kappa \approx 10$, indicative of rapid reaction, regime (d). Table 1 illustrates the differences in overall mass-transport coefficient K_G calculated based on physical dissolution according to H, regime (a); kinetically controlled dissolution according to regime (d); and dissolution under assumption of rapid equilibrium H^*, regime (e). It is seen that reaction to form the hydrate substantially enhances K_G but that assumption of instantaneous equilibrium would lead to erroneously large K_G.

TABLE 1. Evaluation of overall mass-transfer rate coefficient K_G for formaldehyde for three uptake regimes.

Regime (a) Physical Dissolution	Regime (d) Kinetic Dissolution	Regime (e) Equilibrium Dissolution
$\left(\frac{1}{k_G}+\frac{1}{Hk_L}\right)^{-1}$	$\left(\frac{1}{k_G}+\frac{1}{H(k^{(1)}D_{aq})^{1/2}}\right)^{-1}$	$\left(\frac{1}{k_G}+\frac{1}{H^*k_L}\right)^{-1}$
$\left(\frac{1}{1}+\frac{1}{50\times 0.003}\right)^{-1}$	$\left(\frac{1}{1}+\frac{1}{50\times(10\times 10^{-5})^{1/2}}\right)^{-1}$	$\left(\frac{1}{1}+\frac{1}{10^5\times 0.003}\right)^{-1}$
$(1+6.7)^{-1}$	$(1+2)^{-1}$	$(1+0.003)^{-1}$
0.13 cm s^{-1}	0.33 cm s^{-1}	0.997 cm s^{-1}

4.4 Ozone

O_3 is sparingly soluble in water ($H \approx 0.4$). It decomposes only slowly in water but as a strong oxidant it is capable of irreversibly oxidizing dissolved reducing species. The effective first-order rate coefficient $k^{(1)}$ is equal to the sum of the pertinent second-order rate coefficients times species concentrations, but these species and their concentrations are not known *a priori*. Lenschow et al. (1982) and others have reported measurements of O_3 deposition velocity to ocean water ($\approx$ 0.05 cm s^{-1}). Such a value is well less than k_G and also well less than $(1/4)\bar{v}\alpha$ evaluated for the reported value of the mass-accommodation coefficient for O_3 on water, 5×10^{-4}. Consequently atmospheric and interfacial resistance can be neglected. The observed deposition velocity is much greater (factor of 40) than would be expected by physical dissolution alone: $Hk_L \approx 1.2 \times 10^{-3}$ cm s^{-1}. From Equation (9) $K_G = H(k^{(1)}D_{aq})^{1/2}$, from which $k^{(1)} = K_G^2 / H^2 D_{aq} \approx 1.6 \times 10^3$ s^{-1}; i.e., the lifetime of dissolved O_3 in solution is somewhat less than 10^{-3} s. The corresponding distance of penetration of dissolved O_3 into surface water, $(D_{aq} / k^{(1)})^{1/2}$ is approximately 1 μm. This situation is thus an example of a situation in which $K_G << k_G$ yet $A << HG$. The great majority of ozone molecules dissolving in the surface water, $(1-K_G/k_G) \approx 95\%$, return from solution back to the gas phase.

Garland et al. (1980) ascribe the uptake of O_3 by ocean water to reaction with dissolved iodide, for which reaction they must assume a diffusion-controlled second-order rate coefficient of 2×10^9 M^{-1} s^{-1}. Alternatively, the fact that the distance of penetration is so short suggests that reaction might be occurring with organic species that are preferentially concentrated near the interface. This question is not yet resolved, and the mechanism responsible for and controlling this uptake requires further study.

5. CONCLUSION

Rates of dry deposition of gases to surface water (or more generally of air-surface water exchange) vary by orders of magnitude depending on the solubility and aqueous-phase reaction kinetics of the dissolved gas. For non-reactive gases the key parameter is the Henry's law solubility. Interfacial resistance to mass transport does not seem to be significant based upon recent laboratory measurements of mass-accommodation coefficients. For reactive gases a theoretical framework is at hand to quantitatively relate the deposition flux to the chemical reaction rate provided the physical parameters of mass transport and the solubility and kinetic properties of the depositing gas are known. Readily applicable criteria are available to identify controlling processes and thereby allow research efforts to be focussed most appropriately.

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DISCUSSION

J. A. GARLAND. You have treated reversible reactions in some detail. Could you say a few words about irreversible reactions.

S. E. SCHWARTZ. Perhaps I should have been more explicit. Irreversible reactions are simply the limit of reversible reactions where the equilibrium ratio η goes to infinity; this situation is represented by Eq. 9 and by the curve for $\eta = \infty$

in Figure 1. How great η must be for this limit to be attained (to within 10%) is specified by the range of values of κ indicated at Eq. 9.

P. S. LISS. It isn't clear to me why you have restricted yourself to deposition of gases. Much of what you have said is pertinent to evasion from surface water with little change required to cover both situations.

S. E. SCHWARTZ. You are correct. I am afraid that the use of K_G as the independent variable in which the results of the calculations expressed and the examples given reflect my bias in living and conducting my research on the atmospheric side of the interface. It is interesting that a figure plotting overall mass-transfer coefficient against Henry's law coefficient that appears essentially identical to Figure 2 has been given in the context of water evasion rates (R. P. Schwarzenbach and D. M. Imboden, Modelling concepts for hydrophobic organic pollutants in lakes, *Ecological Modelling* **22** 171-212, 1983/84). On closer inspection, however, it turns out that that figure represents a view from the water side. The quantity being plotted is not the overall mass-transfer coefficient referred to the gas-phase concentration, $K_{G,}$ as in the present Figure 2, but the overall mass-transfer coefficient referred to the aqueous-phase concentration, K_L, and that the Henry's law coefficient that serves as the independent variable on the abscissa has the opposite sense of that employed here. Nonetheless the figure looks the same! So yes, the treatment is entirely symmetric, except, of course, that chemical reaction is treated only on the water side.

P. S. LISS. Would you comment on the possibility and likely effect of chemical and biochemical enhancement of CO_2 uptake by the oceans.

S. E. SCHWARTZ. As noted in the text and indicated in Figure 2, the equilibrium ratio of total dissolved C(IV) to CO_2 is substantial at ocean pH, and consequently a corresponding enhancement of the uptake rate might be expected if the reaction rate is sufficiently great. However the laboratory-determined rate of reaction is so slow that it would appear that no enhancement is to be expected. This conclusion is reached also by Smith (S. V. Smith, Physical, chemical and biological characteristics of CO_2 gas flux across the air-water interface, *Plant, Cell and Environment*, **8**, 387-398, 1985), but with the caveat that chemical enhancement might be significant in still (low k_L) eutrophic lakes with pH ≥ 10. A further caveat to this conclusion is the possibility that catalysis by the enzyme carbonic anhydrase present in seawater might enhance the reaction rate sufficiently to lead to an enhancement of the uptake rate. One study (J. C. Goldman and M. R. Dennett, Carbon dioxide exchange between air and seawater: No evidence for rate catalysis, *Science* **220** 199-201, 1983) confirmed that carbonic anhydrase can enhance the uptake rate under certain laboratory conditions but concluded, based on studies with authentic seawater samples, that no such enhancement is to be expected in the ambient environment. Unfortunately the water-side mass transfer coefficients k_L characterizing that study were not specified, so that it is hard to view this conclusion as definitive. A study by Broecker and colleagues (W. S. Broecker, R. Wanninkhof, G. Mathieu, T.-H. Peng, S. Stine, S. Robinson, A. Herczeg and M Stuiver, The radiocarbon budget for Mono Lake: An unsolved mystery, *Earth Planet. Sci. Lett.* **88** 16-26, 1988) rules out inorganic and biological enhancement as causes of apparently high fluxes of $^{14}CO_2$ into a high-salinity, high-alkalinity lake. With respect to improving description of CO_2 uptake on global scales, in my judgment as much or more attention should be focused on the the spatial distribution of the concentration difference $(G - A/H)$ as on the mass transfer coefficient K_G.