

Surface-Specific Reactions on Liquids

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Surface-specific reactivity is included in the theory of gas–liquid reactions. An expression for the reaction probability (fractional loss of a gas-phase species on collision with a liquid surface) is derived and compared to equations derived previously.

Introduction

Surface reactions on a liquid, that is, surface-specific reactions in the interaction of a gas and a liquid, are believed to occur for several heterogeneous reactions including SO₂ hydrolysis,¹ formation of HONO from NO₂,² and the reaction of ClONO₂ with HCl.³ The well-tested theory of gas–liquid interactions^{4,5} takes into account the bulk solution processes of reaction and diffusion but does not include surface reactions. Recently, Hu et al.⁶ and Hanson and Ravishankara³ have incorporated a surface-specific reaction into the kinetics of the uptake of a gas by a liquid, but the applicability of their methods may be restricted because of limiting assumptions^{3,6} or the empirical nature of the equations.⁶ Here, a surface-specific reaction is included in the kinetics of gas–liquid reactions without the limiting assumption of Hanson and Ravishankara.³

The steady-state reaction probability γ (fraction of collisions of a gas-phase molecule with a surface that results in reactive loss) of molecule X was formulated by Hanson and Ravishankara:³

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_b + \Gamma_s} \quad (1a)$$

$$\Gamma_b = \frac{4RTH_X\sqrt{kD}}{\omega} \quad (1b)$$

$$\Gamma_s = \frac{4k_s b'}{\omega} \quad (1c)$$

where α is the mass accommodation coefficient (fraction of collisions with the surface that can lead to incorporation into the bulk liquid), R is the gas constant, T is temperature (K), H_X is the Henry's law coefficient for species X, D is the diffusion coefficient in the solution, k is the first-order loss rate coefficient for X in solution, and ω is the mean thermal speed of X. In the expression for Γ_s , b' is a surface adsorption equilibrium constant (a Langmuir-type constant; that is, in the absence of reaction, the surface concentration of X is proportional to b' times the gas-phase [X]) and k_s is the first-order loss rate coefficient for X on the surface (see appendix of Hanson and Ravishankara³). It was assumed that the surface concentration of X was in equilibrium with the concentration of X in solution just inside the surface.³

Hu et al.⁶ presented an equation based on physical arguments and empirical results that can be written (neglecting their gas-phase diffusion term, γ_{diff} , which is dependent upon experimental conditions):

$$\frac{1}{\gamma} = \frac{1}{\gamma_b(1 - \gamma_s) + \gamma_s} \quad (2a)$$

where

$$\frac{1}{\gamma_b} = \frac{1}{\alpha} + \frac{1}{\Gamma_b} \quad (2b)$$

$$\gamma_s = p_s \frac{C_s a_{[Y]}}{1 + C_s a_{[Y]}} \quad (2c)$$

where p_s is a measured probability, C_s is proportional to the surface reaction rate, and $a_{[Y]}$ is the activity of the reactant Y (already present in/on the liquid). This approach specifically took into account a reduction in the bulk reaction probability γ_b when the surface reaction probability γ_s approaches unity. Note that the time dependent solvation term γ_{sol} in the expression for γ_b given by Hu et al. is equal to zero for steady-state conditions. Also note that p_s is a probability, and thus γ_s is limited to values between 0 and 1.

In both (1c) and (2c), the reaction probability due to a surface-specific reaction depends linearly on the first-order loss rate coefficient on the surface, k_s or $C_s a_{[Y]}$ (for $C_s a_{[Y]} \ll 1$ in eq 2c). Thus a surface-specific reaction will result in γ for species X to vary with reactant Y linearly, and this behavior has been used to discern surface reactions.^{3,6} Conversely, a reaction probability due to reaction in the bulk will vary as the square root of Y (1b). The thickness of the “surface” region is probably a few molecular diameters or less.¹ The surface-specific reaction can be due to an enhanced reaction due to the properties of the surface but can also be used to treat the case when the reacto-diffusive depth⁵ l becomes very small (a few molecular diameters).⁶ In the latter case, additional terms (such as Γ_s or γ_s) could be included as an approximation because the treatment of the liquid as a continuum with bulk processes rather than as discrete molecules is likely to be wrong.

Jayne et al.⁷ presented an equation relating α to the sticking coefficient, S , the fraction of collisions with the surface that result in accommodation on the surface,

$$\alpha = S \frac{k_{\text{sol}}}{k_{\text{sol}} + k_{\text{desorb}}} \quad (3)$$

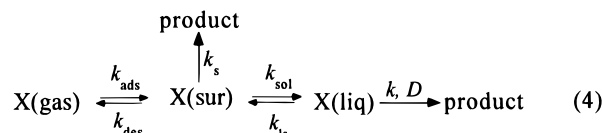
where k_{sol} is the rate coefficient for transfer from the surface into the liquid, and k_{desorb} is the rate coefficient for transfer of the molecule from the surface into the gas phase. Note that S was assumed to be unity and does not appear in their expression. In their work, a first-order loss rate in the interface (on the surface) was not included.

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Here, the steady-state kinetics of uptake of a gas-phase molecule by a liquid where reaction occurs both in the bulk solution and on the surface is considered. The approach previously used by Hanson and Ravishankara³ is modified to include the case when the surface concentration of X, n_s , and the concentration of X in the liquid just inside the surface, $n_l(0)$, are not in equilibrium. Note that gas-phase diffusion and the modification of the gas-kinetic equation when a highly absorbing surface is present⁸ are not taken into account here. These can be treated separately and included when necessary.

Derivation

After Jayne et al.,⁷ with the addition of a first-order loss on the surface, the reactive uptake of X can be represented by



where k_{ads} is the rate coefficient for transfer from the gas to the surface (adsorption), k_{des} is the desorption rate coefficient (surface to gas), k_{sol} is for surface into liquid (solvation), k_{ls} is for liquid to surface, and k_s , k , and D are as defined above. The steady-state concentrations of X on the surface and in the liquid just inside the surface are represented by n_s (molecules/unit area) and $n_l(0)$ (molecules/unit volume), respectively, and the gas-phase concentration of X is n_g (molecules/unit volume).

To solve for the reaction probability, three equations for balancing the flux of X are set up. The gas-kinetic flux times γ is equal to the net flux at the gas–surface interface:

$$\gamma n_g \omega / 4 = n_g k_{\text{ads}} - n_s k_{\text{des}} \quad (5)$$

At steady state on the surface, the difference in the fluxes from gas to surface and from bulk liquid to surface is equal to the number lost per unit time per unit area:

$$n_g k_{\text{ads}} - n_s k_{\text{des}} + n_l(0) k_{\text{ls}} - n_s k_{\text{sol}} = n_s k_s \quad (6)$$

Also, the flux into the bulk liquid (from Fick's first law) equals the net flux between the surface and the liquid:

$$n_s k_{\text{sol}} - n_l(0) k_{\text{ls}} = -D \, dn_l/dz \quad (7a)$$

where dn_l/dz is the gradient of n_l and is evaluated at the surface. Within a semi-infinite planar liquid surface, $n_l(z) = n_l(0) \exp(-z/l)$, where l is the reacto-diffusive length $= (D/k)^{1/2}$ (refs 4, 5). Thus the gradient of $n_l(z)$ evaluated at the surface is $-n_l(0)/l$ and (7a) becomes

$$n_s k_{\text{sol}} - n_l(0) k_{\text{ls}} = D(k/D)^{1/2} n_l(0) = (kD)^{1/2} n_l(0) \quad (7b)$$

The equilibrium constants b' (dimensions of length) and $H' = H_X RT$ (dimensionless) are related to the mass-transfer coefficients between gas, surface, and bulk liquid:

$$b' = k_{\text{ads}}/k_{\text{des}} \quad (8a)$$

$$H' = k_{\text{ads}} k_{\text{sol}} / k_{\text{des}} k_{\text{ls}} = b' k_{\text{sol}} / k_{\text{ls}} \quad (8b)$$

and the (gross) adsorption rate coefficient, k_{ads} , is given by

$$k_{\text{ads}} = S\omega/4 \quad (9)$$

From these equations, the following equation relating the reaction probability to the physical and chemical parameters of

the surface and bulk can be derived (see the Appendix):

$$\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\Gamma_b \frac{k_{\text{des}}}{k_{\text{ls}} + \sqrt{kD}} + \Gamma_s} \quad (10)$$

where Γ_b and Γ_s are given by (1b) and (1c). Note that they are dimensionless, take values ≥ 0 , and are *not* limited to values ≤ 1 . Note eq 10 is valid for a semi-infinite liquid with a planar surface. In the Appendix, an analogous equation for spherical droplets is presented.

Discussion

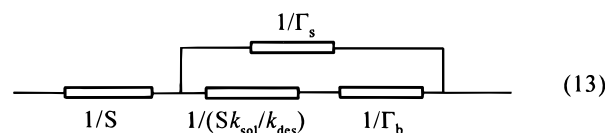
It can be shown, from (1b), (8b), and (9), that

$$\frac{\sqrt{kD}}{k_{\text{ls}}} = \Gamma_b \frac{k_{\text{des}}}{S k_{\text{sol}}} \quad (11)$$

Thus (10) can be rewritten as

$$\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\frac{1}{\Gamma_b} + \frac{1}{S \frac{k_{\text{sol}}}{k_{\text{des}}}} + \Gamma_s} \quad (12)$$

This form is convenient for representing the reaction probability with an electric circuit analogy consisting of a sequence of resistors in series and parallel.^{5,9}



This circuit is similar to that presented by Hu et al.⁶ The main difference is that the $1/\alpha$ resistor of Hu et al. is replaced by two resistors here: $1/S$ and $1/(S k_{\text{sol}}/k_{\text{des}})$. Also, the $1/\Gamma_s$ resistor here is connected at the point where the $1/\alpha$ resistor is split. Note that the equations presented by Hu et al. are not consistent with their resistor model. The resistor model they present would lead to a simple equation $\gamma = \gamma_b + \gamma_s$ (again leaving out γ_{diff}) rather than eq (2a): $\gamma = \gamma_b(1 - \gamma_s) + \gamma_s$. It is not clear whether they were meant to be consistent by these authors. Note that reaction probabilities cannot be described by $\gamma = \gamma_b + \gamma_s$ because $\gamma = 2$ has no meaning in this context (recall that γ_b and γ_s can take values up to 1). Thus the $(1 - \gamma_s)$ term is necessary in their equations.

The circuit analogy for (1a) of Hanson and Ravishankara³ is also similar to (13) except the resistor $1/(S k_{\text{sol}}/k_{\text{des}})$ is not included (resistance of zero) and the resistor $1/S$ is replaced by a resistance of $1/\alpha$. In their derivation, it was explicitly assumed that $n_l(0)$ was in equilibrium with n_s , $n_s k_{\text{sol}} = n_l(0) k_{\text{ls}}$; that is, solvation from liquid to surface (and vice versa) is very fast. This is equivalent to assuming $\alpha = S$. In this case, $k_{\text{ls}} \gg (kD)^{1/2}$ (eq 7b), and from (10) we get (1a) with $\alpha = S$. Thus (1a) derived by Hanson and Ravishankara is equivalent to (10) and (12) with this assumption.

The terms in (10) are much different in form than (2), the equation of Hu et al.⁶ The multiplicative term for Γ_b in (10) does not contain Γ_s (or k_s), and Γ_b and Γ_s are not limited to values less than or equal to unity. Hu et al.⁶ argue that the bulk reaction probability must be reduced when the flux due to the surface reaction dominates that due to bulk reactions. Thus

they include (somewhat arbitrarily they note) the multiplicative factor $(1 - \gamma_s)$ for γ_b . However, in (10) the surface and bulk reaction terms are already “competing” through the coefficients Γ_s and Γ_b : if Γ_s is greater than $\Gamma_b k_{ls}/(k_{ls} + (kD)^{1/2})$, then more loss will occur on the surface than in the bulk and vice versa. In other words, the coefficients correlate with first-order loss processes and “competition” is inherently included. When a surface-specific reaction is rigorously incorporated into the reaction probability, additional terms are not needed to account for a competition between surface and bulk reactions.

The result (12) is equivalent to the previously derived equation for the reaction probability when no surface reactivity is included. When $k_s = 0$, then $\Gamma_s = 0$ and (12) reduces to

$$\frac{1}{\gamma} = \frac{1}{S} \left(1 + \frac{k_{des}}{k_{sol}} \right) + \frac{1}{\Gamma_b} \quad (14)$$

This should be equivalent to the case when only bulk solution properties^{4,5} are considered where

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_b} \quad (15)$$

By comparison of (14) and (15), the mass accommodation coefficient is given by

$$\alpha = S \left(\frac{k_{sol}}{k_{des} + k_{sol}} \right) \quad (16)$$

which is the same expression of Jayne et al.⁷ (eq 3). Note that the expressions of Hu et al.,⁶ (2), and Hanson and Ravishankara,³ (1), reduce to (15) when surface reactions are zero. Also note that when $k_s \neq 0$, the previous formulations (eqs 1³ and 2⁶) use of α instead of S is incorrect (see below). This has little consequence though, as long as they are applied within the scope of the assumptions in the derivations (*e.g.*, ref 3 assumed $\alpha = S$).

The mass accommodation coefficient α does not explicitly appear in (10) or (12), and it may not be a useful parameter for describing the reaction probability when a surface-specific reaction contributes significantly (*i.e.*, when Γ_s is comparable to Γ_b). In this case, the fraction of collisions that leads to incorporation into the bulk liquid will depend upon what fraction is lost on the surface. To avoid this, α should be defined as the fraction of collisions that *can* lead to incorporation into the bulk liquid (α is a measure of the gross flux into the bulk liquid, $\alpha\omega/4$, only in the absence of surface reactions). Therefore, the relation between α and S , (16),⁷ is a defining relation for α . If α and S are known, the ratio k_{sol}/k_{des} , needed in (12) to calculate γ , can be evaluated.

In the present derivation, it is inherently assumed that the surface (and liquid) concentration, n_s , of the molecule (X) being taken up is linearly proportional to the concentration of X in the gas-phase (n_g) via b' and H' , respectively. More precisely, the $n_g k_{ads}$ and $n_l(0)k_{ls}$ terms in eqs 5–7 are assumed to be the gross flux onto the surface for all conditions. This may not be valid for high surface concentrations of X because a significant number of surface sites may be occupied. Thus these terms should be multiplied by a $(1 - \theta)$ factor, where θ is the fractional surface coverage (assuming a Langmuir-type adsorption mechanism). In this case, S and Γ_s are multiplied by the factor $(1 - \theta)$ wherever they appear in eq 12, and γ is a function of θ .

An important assumption in this work is that the reaction probability can be separated into a surface-specific part and a bulk part. For a real liquid, the diffusion coefficient D is probably not constant over the first few molecular layers. Also, the first-order loss rate for X varies from k_s in the surface region of a liquid, which is somewhat arbitrarily defined (see ref 6, for example), to its value in the bulk liquid, k . Therefore, the solution presented here (eqs 10 and 12) should be considered an approximation subject to the scope of the assumptions involved.

Appendix

Addition of (5), (6), and (7b) results in the equation

$$\gamma n_g \omega/4 = n_s k_s + (kD)^{1/2} n_l(0) \quad (A1)$$

and dividing (A1) by n_g results in

$$\gamma \frac{\omega}{4} = \frac{n_s}{n_g} k_s + \sqrt{kD} \frac{n_l(0)}{n_g} \quad (A2)$$

Note that (A1) and (A2) are equal to (A1) and (A5) of Hanson and Ravishankara³ with the identities $n_s = c_i$, $n_g = c_g$, and $n_l(0) = c_0$. Dividing (5) by n_g and including the definitions $k_{ads} = S\omega/4$ and $k_{des} = k_{ads}/b'$, we arrive at an expression for n_s/n_g :

$$\gamma \frac{k_{ads}}{S} = k_{ads} - \frac{n_s}{n_g} k_{des} = k_{ads} \left(1 - \frac{n_s}{n_g} \frac{1}{b'} \right) \quad (5)/n_g$$

$$\frac{n_s}{n_g} = b' \left(1 - \frac{\gamma}{S} \right) \quad (A3)$$

Note that (A3) is equivalent to (A4)¹⁰ of Hanson and Ravishankara³ in the case $\alpha = S$. The ratio $n_l(0)/n_g$ can be obtained by multiplying the ratio $n_l(0)/n_s$ by the ratio n_s/n_g (A3). The ratio $n_l(0)/n_s$ is obtained by dividing (7b) by $n_l(0)$ and rearranging:

$$\frac{n_s}{n_l(0)} k_{sol} - k_{ls} = \sqrt{kD} \quad (7b)/n_l(0)$$

$$\frac{n_l(0)}{n_s} = \frac{k_{sol}}{k_{ls} + \sqrt{kD}} \quad (A4)$$

$$\frac{n_l(0)}{n_g} = \frac{n_l(0)}{n_s} \frac{n_s}{n_g} = \frac{k_{sol}}{k_{ls} + \sqrt{kD}} b' \left(1 - \frac{\gamma}{S} \right) \quad (A5)$$

Substituting (A3) and (A5) into (A2) results in the equation

$$\gamma \frac{\omega}{4} = b' \left(1 - \frac{\gamma}{S} \right) \left(k_s + \sqrt{kD} \frac{k_{sol}}{k_{ls} + \sqrt{kD}} \right) \quad (A6)$$

Dividing both sides by $\gamma\omega/4$ and noting the definitions of Γ_s and Γ_b (eqs 1b and 1c), (A6) becomes

$$1 = \left(\frac{1}{\gamma} - \frac{1}{S} \right) \left(\Gamma_s + \Gamma_b \frac{b'}{H'} \frac{k_{sol}}{k_{ls} + \sqrt{kD}} \right) \quad (A7)$$

From (8b) we note that $b'/H' = k_{ls}/k_{sol}$, whereupon (A7) becomes

$$1 = \left(\frac{1}{\gamma} - \frac{1}{S} \right) \left(\Gamma_s + \Gamma_b \frac{k_{ls}}{k_{ls} + \sqrt{kD}} \right) \quad (\text{A8})$$

from which (10) follows:

$$\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\Gamma_b \frac{k_{ls}}{k_{ls} + \sqrt{kD}} + \Gamma_s} \quad (10)$$

When uptake and reaction is considered on spherical droplets of radius a , the gradient of $n_l(r)$ at the surface, $r = a$, is $n_l(a)[\coth(a/l) - l/a]/l$. Thus the right-hand side of (7b) becomes $(Dk)^{1/2}n_l(a)[\coth(a/l) - l/a]$, $n_l(a)$ is substituted for $n_l(0)$, and the multiplicative factor $f(a/l) = \coth(a/l) - l/a$ appears wherever the $(Dk)^{1/2}$ term appears. In this case, (10) becomes

$$\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\Gamma_b f(a/l) \frac{k_{ls}}{k_{ls} + \sqrt{kD}} + \Gamma_s} \quad (\text{A9})$$

The equivalent expression, (12), becomes for spherical droplets of radius a

$$\frac{1}{\gamma} = \frac{1}{S} + \frac{1}{\frac{1}{\Gamma_b f(a/l)} + \frac{1}{S(k_{sol}/k_{des})} + \Gamma_s} \quad (\text{A10})$$

References and Notes

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- (10) Equation A4 of ref 3 contains a "normalization" error. The quantity p_i^*/RT should be p_i^* because p_i^* ($=c_i/b'$) is taken to have the same units as c_g . Equations A5–A7 are correct ("normalized") as written in ref 3.