



Desorption Rates at Electrode/Electrolyte Interfaces

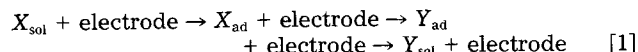
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ABSTRACT

A recently proposed theoretical approach using classical stochastic diffusion theory (CSDT) to predict desorption rates from solid surfaces is generalized to treat desorption of a particle from a solid surface into a liquid phase. Such systems are characterized by large friction constants resulting in a strong dependence of the desorption rate on the microscopic parameters of the liquid (e.g., solvent self-diffusion constant). The dependence of desorption on the different microscopic parameters of the system is examined. Based on these results, we propose electrochemical measurements which can be combined with the CSDT method to obtain microscopic information on the particle-surface interaction potentials at the solid/liquid interface.

The understanding of the microscopic details of processes occurring at metal and semiconductor electrodes have great importance in the design and improvement of electrochemical cells, fuel cells, etc., as well as in the fundamental study of solid/liquid interfaces. The basic and most important step in any system that contains a solid/liquid interface is the charge transfer process. Although a large amount of work has been devoted to the study of charge transfer at electrodes, relatively little is known about the detailed microscopic dynamics of these processes. The rate of charge transfer at an electrode can be regarded, in general, as a combination of the rates of three basic steps; (i) adsorption to the electrode surface, (ii) charge or atom transfer between the adsorbate and the electrode, and (iii) desorption of the newly formed adsorbate from the surface to the solvent. We can write these three steps in the following schematic form



where the subscripts sol and ad stand for solvated and adsorbed, respectively, and it was assumed that particle X was transformed into Y after the charge transfer takes place. In general, it is impossible to measure experimentally the individual rates of these three processes. Theoretical determination of the charge transfer rate, $X_{\text{ad}} + \text{electrode} \rightarrow Y_{\text{ad}} + \text{electrode}$, is possible provided that the adsorbate-electrode interaction potentials and the corresponding coupling terms are known. However, since the adsorption and desorption steps are complicated many-body processes that take place on a very long time scale compared to a molecular vibrational period, a theoretical estimate of the corresponding rates is very difficult.

Recently we have described a new method to evaluate rates of desorption for atoms and molecules adsorbed on solid surfaces, which is based on classical stochastic diffusion theory (CSDT) (1). Using the CSDT formalism (in the following we shall refer to Ref. (1b) as paper I), we have derived simple analytic expressions for atoms and molecules desorbing from solid surfaces (to vacuum), where the desorption rates were given in terms of the microscopic parameters of the system (e.g., D_e , the binding energy, Ω_0 , the stretching frequency of the adsorbate-surface interaction, k_r , the force constant for frustrated rotation, and T , the temperature). Similar expressions for the rate of desorption of both atoms (2) and molecules (3) from solid surfaces have also been obtained using transi-

tion state theory (TST). These rate expressions have the form

$$R = \frac{\Omega_0}{2\pi} f(T) \exp \left[- \frac{D_e}{kT} \right] \quad [2]$$

where $f(T) = 1$ for atomic adsorbate and $f(T) \propto k_r/kT$ for molecules. An interesting feature of Eq. [2] is that the desorption rate does not depend on the characteristics of the solid surface (e.g., Debye frequency) except through the adsorbate-surface interaction potential. This behavior is a result of the thermal averaging, incorporated in both the CSDT and TST methods, which suppresses the individual dynamical events occurring during the desorption process.

In this paper, we derive an expression for the rate of desorption of an atom (or ion) from an electrode surface into a condensed phase, namely, the solution. In so doing, we shall follow a derivation similar to the one employed in gas phase desorption (1). An expression for the desorption rate is derived below followed by the presentation and discussion of the results obtained for some model calculations. Finally, in the last part of the paper we outline some conclusions related to the calculated rates.

CSDT for Desorption from Electrode Surfaces

We shall start by considering a system composed of a desorbing particle (atom or ion), with mass M , interacting with a solid surface (electrode) and a number of solvent particles, with mass M_1 , as illustrated schematically in Fig. 1. For the description of the surface, we shall follow the ideas introduced by Adelman and Doll (4, 5) and divide the electrode atoms into two groups: (i) a small number of atoms which are strongly interacting with the adsorbed particle, this group will be called the primary zone, and (ii) the rest of the solid which is assumed to act as a heat bath. Without loss of generality we shall assume that the primary zone contains only one atom whose mass will be denoted by M_s . A further simplification is introduced by limiting both the desorbing particle and the primary zone atom to a one-dimensional motion normal to the solid surface. Thus, the motion of the adparticle will be described by a Newtonian equation of motion

$$M\ddot{R} = - \frac{\partial V(R, \zeta, \mathbf{Z})}{\partial R} \quad [3]$$

where ζ represents the displacement of the surface pri-

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mary zone atom from its lattice point. The vector \mathbf{Z} includes the displacement from equilibrium along the line connecting the centers of the adparticle and the solvent particles surrounding it. The total interaction potential, $V(R, \zeta, \mathbf{Z})$, felt by the adparticle is assumed to be given by a sum of pairwise interactions

$$V(R, \zeta, \mathbf{Z}) = V(R - \zeta) + \sum_{i=1}^{N(R)} V_i(R - \mathbf{Z}_i) \quad [4]$$

where $N(R)$ is the number of solvent particles surrounding the adsorbate at any given R . In the following, we shall use harmonic potentials to represent the interaction between the desorbing particle and the solvent

$$V_i(R - \mathbf{Z}_i) = 1/2 k_i [r - \mathbf{Z}_i]^2 \quad [5]$$

The interaction between the surface and the desorbing particle will be represented by a properly dissociating potential (e.g., Morse or Lennard-Jones) which is fitted with parabolic splines (see paper I)

$$V(R - \zeta) = \sum_i V_i(x) \quad [6]$$

where $x = R - \zeta$ and

$$V_i(x) = \begin{cases} 0 & x < x_i \\ A_i + B_i x + 1/2 C_i x^2 & x_i \leq x \leq x_{i+1} \\ 0 & x_{i+1} < x \end{cases} \quad [7]$$

x_i and x_{i+1} being the boundaries of the i th interval. The fit of Eq. [7] is performed in such a way that at any boundary point, x_i , the functions V_{i-1} and V_i and their first derivatives are continuous.

The motion of the surface primary zone atom as well as the motion of the solvent molecules will be described using the equivalent harmonic chain representation (EHCR) introduced by Adelman (6). We shall use this representation to construct model heat baths and employ the Markovian approximation in reducing the resulting generalized Langevin equations of motion to the corresponding Langevin equations (Appendix A). The introduction of the Markovian approximation is justified (see paper I) due to the large difference in the desorption time scale compared to a molecular vibrational period. Using the effective equation of motion derived in Appendix A to describe the motion of the primary zone surface atom, we have

$$M_s \ddot{\zeta} = -M_s \Omega_s^2 \zeta - M_s \beta_s \dot{\zeta} - \frac{\partial V(R, \zeta, \mathbf{Z})}{\partial \zeta} + f_s(t) \quad [8]$$

and similarly, the motion of the i th solvent particle is described by

$$M_i \ddot{\mathbf{Z}}_i = -M_i \Omega_i^2 \mathbf{Z}_i - M_i \beta_i \dot{\mathbf{Z}}_i - \frac{\partial V(R, \zeta, \mathbf{Z})}{\partial \mathbf{Z}_i} + f_i(t) \quad [9]$$

The effective frequencies and friction constants of Eq. [8] and [9] are given in terms of the EHCR parameters as discussed in Appendix A.

Next we substitute the potentials of Eq. [2]-[7] into Eq. [8] and [9] and solve them formally (using Laplace transforms). These solutions are then substituted into Eq. [3] to give

$$M \ddot{R} = \sum_{i=1}^{N(R)} \left[-k_i R + \frac{k_i^2}{M_i} \int_0^t \Theta_i(t-t') R(t') dt' + k_i f_i(t) \right] + \sum_{i=1}^n \left[-(B_i + C_i R) + C_0 \frac{C_i}{M_s} \int_0^t \Theta_s(t-t') R(t') dt' + C_i f_s(t) \right] \chi_i \quad [10]$$

where C_0 represents the force constant associated with the desorbing particle-surface interaction and χ_i is the characteristic function of the i th interval ($\chi_i = 1$ if R is in the i th interval and $\chi_i = 0$ otherwise). The memory kernels Θ_i and Θ_s in Eq. [10] are given by

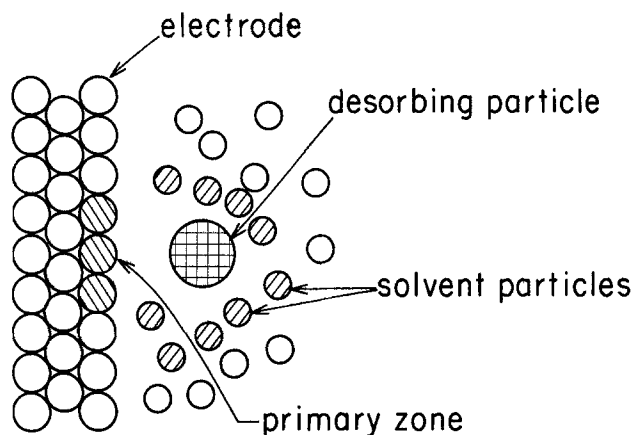


Fig. 1. Schematic description of the adsorbate at a solid/liquid interface.

$$\Theta_i(t) = \frac{1}{S_i} \left\{ \exp \left[-\frac{1}{2} (\beta_i - S_i) t \right] - \exp \left[-\frac{1}{2} (\beta_i + S_i) t \right] \right\} \quad [11]$$

where $S_i = [\beta_i^2 - 4\bar{\Omega}_i^2]^{1/2}$ and $\bar{\Omega}_i^2 = \Omega_i^2 + k_i/M_i$. Similarly

$$\Theta_s(t) = \frac{1}{S_s} \left\{ \exp \left[-\frac{1}{2} (\beta_s - S_s) t \right] - \exp \left[-\frac{1}{2} (\beta_s + S_s) t \right] \right\} \quad [12]$$

where $S_s = [\beta_s^2 - 4\bar{\Omega}_s^2]^{1/2}$ and $\bar{\Omega}_s^2 = \Omega_s^2 + C_0/M_s$.

Assuming that the adsorbate-solvent interaction has the same form for all the $N(R)$ solvent particles, we can eliminate the first summation in Eq. [10] and instead multiply each term by $N(R)$. Furthermore, we may also eliminate the second summation and replace C_i and B_i by $C(R)$ and $B(R)$. Integrating by parts the two convolution integrals in Eq. [10] and rearranging terms, we can rewrite the effective equation of motion for the desorbing particle as

$$M \ddot{R} = -\{[N(R)k_i - \Gamma_i(0)] + [C(R) - \Gamma_s(0)]\}R - B(R) - \int_0^t [\Gamma_i(t-t') + \Gamma_s(t-t')] \dot{R}(t') dt' - [\Gamma_i(t) + \Gamma_s(t)] R(0) + F(t) \quad [13]$$

where

$$\Gamma_i(t) = N(R) \frac{k_i^2}{M_i} \int_t^\infty \Theta_i(t') dt' \quad [14]$$

$$\Gamma_s(t) = \frac{C_0 C(R)}{M_s} \int_t^\infty \Theta_s(t') dt' \quad [15]$$

The term in braces in Eq. [13] represents the total potential felt by the desorbing particle. It includes the corrections due to the thermal motion of both the surface atoms and the solvent particles surrounding the desorbing particle; thus, this is the potential that one would obtain experimentally. In the following, we shall denote this total potential by $V_{\text{tot}}(R, \zeta, \mathbf{Z})$. Due to the large difference in time scales one may introduce the Markovian limit to Eq. [13] and obtain the corresponding Langevin equation

$$M \ddot{R} = -\frac{\partial V_{\text{tot}}(R, \zeta, \mathbf{Z})}{\partial R} - (\tilde{\beta}_i(R) + \tilde{\beta}_s(R)) \dot{R} + \tilde{F}(t) \quad [16]$$

where

$$\tilde{\beta}_i(R) = \frac{N(R)k_i^2\beta_i}{M_i\bar{\Omega}_i^4} \quad [17]$$

$$\tilde{\beta}_s(R) = \frac{C_0 C(R)\beta_s}{M_s\bar{\Omega}_s^4} \quad [18]$$

Equation [16] represents an effective equation of motion for the desorbing particle whose motion is coupled to a heat bath constituted by the electrode surface

and the solvent particles. Since $V_{tot}(R, \zeta, \mathbf{Z})$ is an anharmonic function, we may fit it by a parabolic spline fit of the form introduced in Eq. [4]-[7]

$$V_{tot}(R, \zeta, \mathbf{Z}) = \sum_i V_i(R) \quad [19]$$

$$V_i(R) = \begin{cases} 0 & R < R_i \\ A_i + \bar{B}_i R + \frac{1}{2} \bar{C}_i R^2 & R_i \leq R \leq R_{i+1} \\ 0 & R_{i+1} < R \end{cases} \quad [20]$$

To express $\bar{\beta}_1$ and $\bar{\beta}_s$ in terms of the microscopic parameters of the system, one should evaluate the effective frequencies and friction constants of Eq. [8] and [9]. One can use as an estimate of these quantities the expressions obtained in Appendix A (Eq. [A.7] and [A.9]) and rewrite β_1 and β_s in the form

$$\bar{\beta}_1 = \frac{N(R)kT\kappa_1^2}{D_1 M_1^2 \left(\Omega_{01}^2 + \frac{\kappa_1}{M_1} \right)^2} \quad [21]$$

where D_1 is the self-diffusion coefficient of the liquid, and

$$\bar{\beta}_s = \frac{0.52547 \omega_D C_0 C(R)}{M_s \left(0.33295 \omega_D^2 + \frac{C_0}{M_s} \right)^2} \quad [22]$$

Thus, the final effective equation of motion for the desorbing particle is given by

$$M\ddot{R} = -\bar{B}(R) - \bar{C}(R)R - \beta_{tot}(R)\dot{R} + \tilde{F}(t) \quad [23]$$

where $\bar{B}(R)$ and $\bar{C}(R)$ are the first and second derivatives of the total potential, V_{tot} , evaluated at the point R , and $\beta_{tot}(R) = \bar{\beta}_1(R) + \bar{\beta}_s(R)$.

As discussed above, Eq. [23] describes the motion of the desorbing particle in terms of a Brownian oscillator where the interaction with the heat bath is given in terms of the microscopic quantities of the system. The amplitude of the random force, $\tilde{F}(t)$, is defined by its relation to β_{tot} through the second fluctuation-dissipation theorem. To derive an expression for the rate of desorption, one should first evaluate the probability distribution function for the desorbing particle and use this to obtain the flux at any given point in space. In evaluating the expression for the flux, we shall closely follow the derivation in paper I. The steady-state probability distribution is the solution to the (time independent) generalized Liouville equation (1, 7) and is given by

$$W(R, U) = A_0 F(R, U) \exp \left[-\frac{MU^2}{2kT} - \frac{V_{tot}(R)}{kT} \right] = A_0 F(R, U) W_{MB}(R, U) \quad [24]$$

where A_0 is a normalization constant, U is the velocity of the desorbing particle, W_{MB} is the Maxwell-Boltzman distribution function, and

$$F(R, U) = \left[\frac{\alpha - \tilde{\beta}_{tot}}{2\pi q} \right]^{\frac{1}{2}} \int_0^\xi \exp \left[-\frac{(\alpha - \tilde{\beta}_{tot})\xi^2}{2q} \right] d\xi' \quad [25]$$

where $\xi = U - \alpha R - b$, $q = kT\tilde{\beta}_{tot}$, $\tilde{\beta}_{tot} = \beta_{tot}/M$ and

$$\alpha = \frac{1}{2}[\tilde{\beta}_{tot} + (\tilde{\beta}_{tot}^2 - 4d_1)^{\frac{1}{2}}] \quad [26]$$

$$b = -\frac{2d_0}{\alpha - \tilde{\beta}_{tot}} \quad [27]$$

where $d_1 = \bar{C}(R)/M$ and $d_0 = \bar{B}(R)/M$. The functional form of $F(R, U)$ is such that $F(R, U) = 1$ for $R = 0$ while $F(R, U) \rightarrow 0$ as $R \rightarrow \infty$.

In order to obtain an expression for the rate of desorption, we will calculate the flux of desorbing particles at a given distance from the surface, R_0 . The calculated flux must take into account only those particles at R_0 which have sufficient kinetic energy (and the proper velocity direction) to escape. Thus, the expression for the flux at a given value of R_0 is

$$j(R_0, U_0) = \int_{U_0}^\infty W(R_0, U) U dU \quad [28]$$

where U_0 is the smallest (positive) velocity for which a particle at R_0 will desorb, i.e.

$$D_e = V_{tot}(R_0) + \frac{1}{2}MU_0^2 \quad [29]$$

and where D_e is the well depth of V_{tot} . Substitution of Eq. [24] and [25] into [28] gives

$$j(R_0, U_0) = A_0 \left(\frac{\alpha - \tilde{\beta}_{tot}}{2\pi q} \right)^{\frac{1}{2}} \exp \left[-\frac{V_{tot}(R_0)}{kT} \right] \times \int_{U_0}^\infty \exp \left[-\frac{MU^2}{2kT} \right] \int_0^\xi \exp \left[-\frac{(\alpha - \tilde{\beta}_{tot})\xi^2}{2q} \right] d\xi' U dU \quad [30]$$

Integrating by parts and rearranging we obtain

$$j(R_0, U_0) = A_0 \frac{kT}{M} \exp \left\{ -\frac{[MU_0^2 + 2V_{tot}(R_0)]}{2kT} \right\} Y(T) \quad [31]$$

where

$$Y(T) = \Phi(\alpha_1) + \exp(-\eta) \left[\frac{\pi\beta_{tot}kT}{2Ma} \right]^{\frac{1}{2}} [1 - \Phi(\alpha_2)] \quad [32]$$

$$\text{with } \alpha_1 = \left(\frac{M(\alpha - \beta_{tot})}{2kT\beta_{tot}} \right)^{\frac{1}{2}} [U_0 - (\alpha R_0 + b)] \quad [33]$$

$$\alpha_2 = \left(\frac{Ma}{2kT\beta_{tot}} \right)^{\frac{1}{2}} [-\vartheta(\alpha R_0 + b) + U_0] \quad [34]$$

$$\vartheta = 1 - \beta_{tot}/\alpha \quad [35]$$

and

$$\eta = \vartheta\beta_{tot}(\alpha R_0 + b)^2/2q \quad [36]$$

The symbol $\Phi(\alpha)$ represents the error function (8). Substituting Eq. [29] into Eq. [31]-[32] leads to the final expressions for the flux

$$j(R_0, U_0) = A_0 \frac{kT}{M} Y(T) \exp \left[-\frac{D_e}{kT} \right] \quad [37]$$

The rate for a desorption process is given (1, 7) by the ratio of the flux (Eq. [31]-[32]) at R_0 to the number of particles, N_0 , at the surface. The distribution function of the particles in the neighborhood of the equilibrium distance, $R = 0$, is given by W_{MB} , Eq. [24], leading to

$$N_0 = A_0 \int_{-\infty}^\infty \int_{-\infty}^\infty \exp \left[-\frac{MU^2}{2kT} - \frac{V_{tot}(R)}{kT} \right] dR dU = A_0 \left[\frac{2\pi kT}{M} \right]^{\frac{1}{2}} \int_{-\infty}^\infty \exp \left[-\frac{V_{tot}(R)}{kT} \right] dR \quad [38]$$

where the limits in the integral over R have been taken from $-\infty$ to ∞ because the integrand becomes negligibly small for values of R far away from $R = 0$.

For experimentally interesting temperature ranges (where $kT \ll D_e$), one can approximate the interaction potential, $V_{tot}(R)$, by a harmonic potential to obtain

$$N_0 = A_0 \left(\frac{2\pi kT}{M\Omega_0} \right) \quad [39]$$

where Ω_0 is the stretch frequency associated with the bottom of the potential well, V_{tot} .

Combining Eq. [37] and [38] leads to a desorption rate of the form

$$R = \frac{j}{N_0} = \left[\frac{kT}{2\pi M} \right]^{\frac{1}{2}} Y(T) \left\{ \int_{-\infty}^\infty \exp \left[-\frac{V_{tot}(R)}{kT} \right] dR \right\}^{-1} \exp \left[-\frac{D_e}{kT} \right] \quad [40]$$

and using Eq. [39] for N_0 leads to

$$R = \frac{\Omega_0}{2\pi} Y(T) \exp \left[-\frac{D_e}{kT} \right] \quad [41]$$

as the final expression for the desorption rate of atoms from solid surfaces.

In concluding this section, it should be emphasized that the major assumptions in deriving the expressions for the desorption rate are the introduction of the Markovian limit in Eq. [30] and [A.4]. As discussed above, the justification for the use of this approximation is based on the large difference between the time scale for the process of interest (desorption) compared to the molecular time scale (the vibrational period). Namely, we have assumed that the long time behavior of the different motions is well described by the Langevin equation of motion. It should be noted that a similar derivation can be made for this case in which Eq. [30] and [A.4] are used without the introduction of the Markovian approximation. Such derivation is much more complicated, due to the algebraic complexity of the equations. At present, we are in the process of performing these calculations to check the validity of the use of the Markovian limit.

Results and Discussion

In this section, we shall discuss the dependence of the desorption rate on the different microscopic parameters of the system. One of the major difficulties in most microscopic theories of solid/liquid interfaces arises from the lack of reliable interaction potentials for such systems. In the present study, we have chosen a model potential of the Morse type. One of our main objectives will be the study of the relationship of desorption rates to the potential parameters (D_e and Ω_0). Moreover, in the calculations described below, we have introduced a further approximation, namely, we assumed that $\Omega_{0(D)}^2 \ll k_f/M_i$. Since $\Omega_{0(D)}$ corresponds to the low frequency limit (it is zero for the case of free diffusion), this assumption is valid for most systems (especially in the case where the adsorbate-solvent interaction is strong, e.g., for ions in polar solvents). Using this approximation, we can rewrite the friction due to the solvent (Eq. [21]) in the form

$$\tilde{\beta}_1 = \frac{N(R)kT}{D_1} \quad [42]$$

A comparison between the magnitudes of $\tilde{\beta}_1$ in Eq. [42] and $\tilde{\beta}_s$ of Eq. [22] for typical values of the different parameters show that $\tilde{\beta}_s$ is smaller than $\tilde{\beta}_1$ by about two to four orders of magnitude (for example, for $M_s = 50$, $\Omega_0 = 600 \text{ cm}^{-1}$, $D_1 = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $T = 300 \text{ K}$, $\omega_0 = 278 \text{ cm}^{-1}$, and $R = 6.0 \text{ bohr}$, we obtain $\tilde{\beta}_1 = 38.6 \text{ a.u.}$ and $\tilde{\beta}_s = 0.36 \text{ a.u.}$). As a result, one may neglect $\tilde{\beta}_s$ and write

$$\beta_{\text{tot}}(R) = \tilde{\beta}_1(R) \quad [43]$$

In obtaining Eq. [43], we have taken into account the fact that $C(R)$ at $R = R_0$ is smaller than C_0 by about two orders of magnitude.

In Fig. 2, we present the calculated desorption rate as a function of temperature for two different values of Ω_0 (all other parameters are kept constant). In both cases, the solid line represents the actual rate while the dashed line represents the rate that one would obtain by setting $Y(T) = 1$. It is clear from these results that $Y(T)$ is very sensitive to changes in the stretch frequency while its dependence on the variation in T is weak. Moreover, it is clear from the functional form of Y (Eq. [32]) that this quantity will tend to reduce the desorption rate into a liquid with respect to that into vacuum. Figure 3 shows the variation of $\log(Y)$ as a function of the mass of the adparticle for different frequencies and bond strength of the total potential. This figure shows that $Y(T)$ exhibits a strong dependence on M , Ω_0 , and D_e , while it is weakly dependent on both D_1 (in the physically meaningful range of the diffusion constant, $5 \times 10^{-6} - 5 \times 10^{-5}$) and T .

Under typical electrochemical experimental conditions, it is difficult to change the temperature in the controlled manner (temperature programmed desorption) so useful at the gas/solid interface, but systematic changes in the applied voltage are very easy to perform. To relate our theory to these conditions, we have calculated the varia-

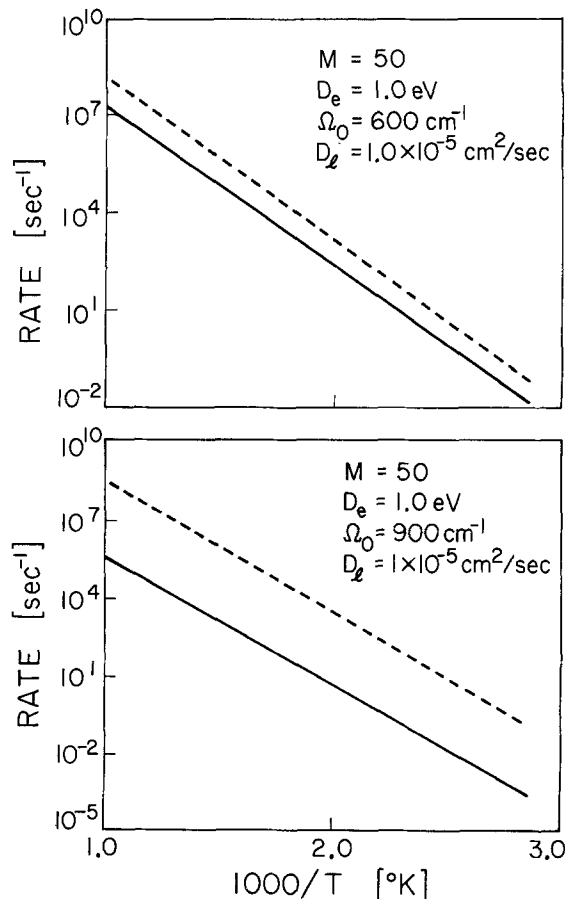


Fig. 2. Rates of desorption vs. temperature for two different stretch frequencies (a, top) $\Omega_0 = 600 \text{ cm}^{-1}$ and (b, bottom) $\Omega_0 = 900 \text{ cm}^{-1}$. The solid line corresponds to the calculated rate while the dashed line represents the rate that would be obtained by setting $Y(T) = 1$.

tion of the desorption rate as a function of the applied voltage. In the absence of an external field, the potential felt by the desorbing particle, V_{tot} , was assumed to have a Morse form. The potential profile due to the applied field through the diffuse layer was chosen to vary according the Gouy-Chapman (9) model

$$V_{\text{elec}}(X) = 2kT \{ \log(1 + A(V_0) \exp[-\alpha X]) - \log(1 - A(V_0) \exp[-\alpha X]) \} \quad [44]$$

where $1/\alpha = 30.4 \text{ \AA}$, X is the distance from the electrode and

$$A(V_0) = \tanh\left(\frac{V_0}{4kT}\right) \quad [45]$$

V_0 being the potential difference between the electrode and the bulk of the solution. We then assumed that the net potential felt by the adparticle (considered to be an ion in this case) is given by

$$V_{\text{net}} = V_{\text{tot}} + V_{\text{elec}} \quad [46]$$

Figure 4 shows the dependence of the desorption rate on the applied voltage. It is evident from these results that there is a large change in the rate (about three orders of magnitude) at low applied fields, and one obtains a saturation at voltages that are larger than 0.3 V . This saturation is a result of the fast exponential decay of $V_{\text{elec}}(X)$ at high voltages. The increase in the rate is a consequence of our choice of the sign of the potential difference between the two electrodes. A decrease in the rate would be obtained if we would choose a reversed sign for this potential difference.

Conclusions

We have described in this paper a microscopic model which leads to analytic expressions for the desorption

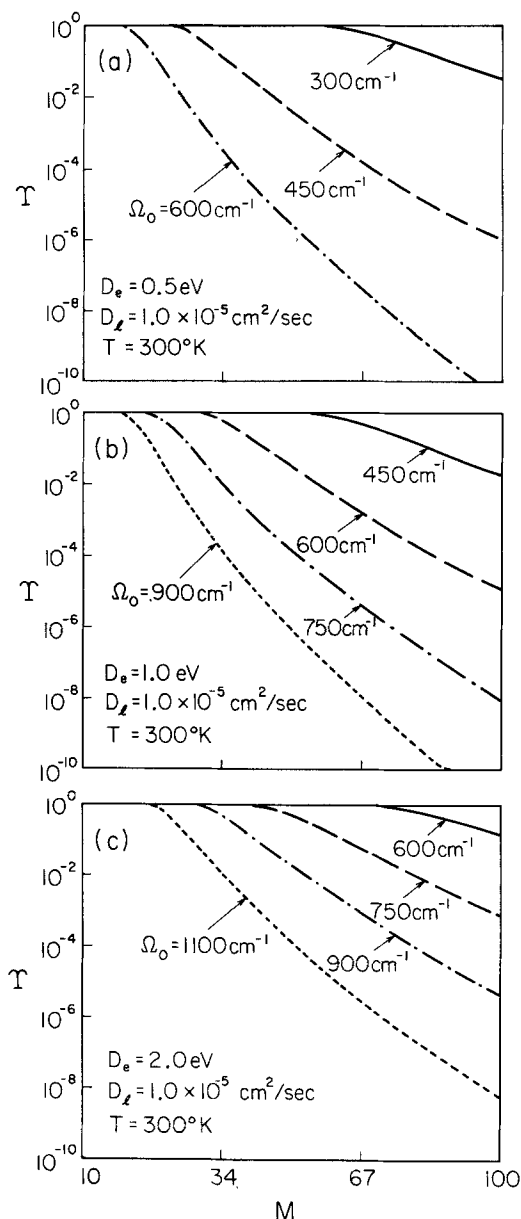


Fig. 3. Variation of $Y(T)$ with the adsorbate mass for different dissociation energies. (a, top) $D_e = 0.5$ eV; (b, middle) $D_e = 1.0$ eV; and (c, bottom) $D_e = 2.0$ eV.

rate of an adsorbate from an electrode into the solvent. These expressions are easy to implement, provided that the microscopic parameters of the system are known. We have also proposed a procedure to calculate the dependence of the desorption rate on an applied electric field. Unfortunately, the microscopic details of processes that occur at electrode/electrolyte interfaces are very difficult to obtain experimentally, and hence, it is necessary to link these microscopic quantities to experimentally measurable data. A possible example corresponds to the measurement of the equilibrium rate constant (ratio between adsorption and desorption rates), which can then be used to obtain estimates of the adparticle-electrode binding energy. For example, one could obtain the equilibrium rate constant from measurements of the variation of the flatband potential, $V_H(C_{tot})$, of semiconductor electrodes as a function of ion concentration, C_{tot} (10). Consider a parallel plate capacitor model of the interface. The surface charge density, $\sigma(C_{tot})$, can be obtained by using the Schottky model of a metal-semiconductor junction (11),

$$\sigma(C_{tot}) = [2e\epsilon N_D V_H(C_{tot})]^{1/2} \quad [47]$$

where e is the fundamental charge, ϵ is the dielectric constant, and N_D is the impurity concentration in the semiconductor. If one assumes that the change in flatband

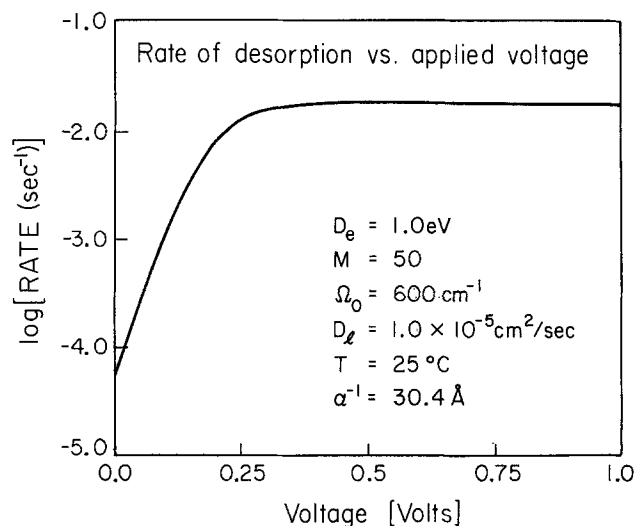


Fig. 4. Rate of desorption vs. applied voltage

potential as a function of the concentration of ions in the solution is mainly due to adsorption of ions on the electrode surface, then the adsorbate concentration in the Helmholtz layer, C_{ad} (number of particles per unit volume), is given by

$$C_{ad} = \frac{[\sigma^2(0) + 2e\epsilon N_D \Delta V_H]^{1/2} - \sigma(0)}{ed} \quad [48]$$

where d is the width of the Helmholtz layer, and $\sigma(0)$ corresponds to the surface charge density when $C_{tot} = 0$. In Eq. [48], we assumed that the adsorption of ion on the electrode surface does not change the initial surface charge density, that is

$$\sigma(C_{tot}) \approx edC_{ad} + \sigma(0) \quad [49]$$

This assumption should be particularly applicable at low coverages of the electrode surface. Equation [48] relates the measured change in flatband potential, ΔV_H , to C_{ad} . Assuming equilibrium conditions for a given C_{tot} , we have

$$C_{ad}k_d = (C_{tot} - C_{ad})k_{ad} \quad [50]$$

where k_d and k_{ad} are the rates for desorption and adsorption, respectively. Equations [48] and [50] provide a means to determine the equilibrium constant of the system, k_{ad}/k_d , from measurements of C_{tot} and ΔV_H , as a function of applied voltage.

Once the equilibrium constant is known, one could use the results of CSDT (Eq. [41]) to determine the adparticle-electrode binding energy, D_e , as follows. From a knowledge of the vibrational frequencies for the adsorbate-electrode system (e.g., from IR reflection experiments) and an independent determination of the adsorption rate, k_{ad} , (e.g., by using Langmuir adsorption-desorption kinetics), one would determine the binding energy from Eq. [50] and [41].

Acknowledgment

We acknowledge partial support of this work by the Department of Energy (Contract DE-AM03-76SF00767; Project Agreement DE-AT03-80ER10608).

Manuscript submitted Aug. 1, 1983.

APPENDIX A

In this appendix we shall outline the procedure by which the parameters of the Langevin equations of motion (Eq. [8] and [9]) can be evaluated. We start by describing the motion of the primary zone surface atom and the motion of a solvent particle using the equivalent harmonic chain representation introduced by Adelman (6). For simplicity, we shall use a two atom model heat bath chain

$$\begin{aligned} \ddot{Q}_0(t) &= -\omega_{e1}^2 Q_0(t) + \omega_{e1}^2 Q_1(t) \\ \ddot{Q}_1(t) &= -\Omega_1^2 Q_1(t) + \omega_{e1}^2 Q_0(t) - \beta_2 \ddot{Q}_1(t) + f_2(t) \end{aligned} \quad [A-1]$$

where Q_0 is the actual position of the particle, and Q_1 is the position of a fictitious particle. The coefficients ω_{e0}^2 and ω_{c1}^2 represent the Einstein and coupling frequencies while Ω_1^2 and β_2 are the low frequency and friction constant, respectively. Reference (6) provides a description of the derivation and the relations between these parameters. We now solve formally (using Laplace transforms) the equation of motion for Q_1 and substitute the result in the equation for Q_0

$$\ddot{Q}_0(t) = -\omega_{e0}^2 Q_0(t) + \omega_{c1}^4 \int_0^t \Theta(t-t') Q_0(t') dt' + \tilde{f}(t) \quad [A-2]$$

where

$$\Theta(t) = \frac{1}{S} \{ \exp(-\frac{1}{2}(\beta_2 - S)t) - \exp[-\frac{1}{2}(\beta_2 + S)t] \} \quad [A-3]$$

and $S = [\beta_2^2 - 4\Omega_1^2]^{\frac{1}{2}}$. Integration by parts of the memory integral of Eq. [A-2] yields

$$\ddot{Q}_0(t) = -\omega_{e0}^2 Q_0(t) + \omega_{c1}^4 \beta(0) Q_0(t) - \omega_{c1}^4 \int_0^t \beta(t-t') \dot{Q}_0(t') dt' - \omega_{c1}^4 Q_0(0) \beta(t) + \tilde{f}(t) \quad [A-4]$$

where $\beta(t)$ is related to Θ by

$$\beta(t) = \int_t^\infty \Theta(t') dt' \quad [A-5]$$

We introduce now the Markovian limit to reduce Eq. [A-4] into a Langevin equation of the form

$$\ddot{Q}_0(t) = -\Omega_{\text{eff}}^2 Q_0(t) - \beta_0 \dot{Q}_0(t) + F(t) \quad [A-6]$$

where the frequency and friction constants are given by

$$\Omega_{\text{eff}}^2 = \omega_{e0}^2 - \frac{\omega_{c1}^4}{\Omega_1^2} \quad [A-7]$$

and

$$\beta_0 = \frac{\omega_{c1}^4 \beta_2}{\Omega_1^4} \quad [A-8]$$

Thus, Eq. [A-6] represents an effective equation of motion which governs the motion of both the primary zone surface atom and the solvent particle. The coefficients in these equations of motion are given in term of the equivalent harmonic chain representation parameters which for a Debye solid take the values (6): $\omega_{e0}^2 = 0.6 \omega_D^2$, $\omega_{c1}^2 = 0.262 \omega_D^2$, $\Omega_1 = 0.507 \omega_D$, and $\beta_2 = 0.161 \pi \omega_D$. Using these values for the EHCR parameters, we obtain that

$$\Omega_{\text{eff}}^2(\text{solid}) = 0.33295 \omega_D^2 \quad [A-9]$$

and

$$\beta_0(\text{solid}) = 0.52547 \omega_D \quad [A-10]$$

It is much more difficult to estimate the EHCR parameters for a liquid particle since a knowledge of the velocity autocorrelation function is required. However, we may use the relation (6)

$$\Omega_1^2 = \frac{\omega_{c1}^4}{\omega_{e0}^2 - \Omega_0^2} \quad [A-11]$$

and

$$\beta_2 = \beta_1 \frac{\Omega_1^2}{\omega_{e0}^2 - \Omega_0^2} \quad [A-12]$$

where we used the Einstein relation $\beta_1 = kT/M_1 D_1$ (k = Boltzmann factor, M_1 = solvent particle mass, and D_1 = self-diffusion constant of the solvent). One can use these relations to rewrite Ω_{eff}^2 and β_0 in the form

$$\Omega_{\text{eff}}^2 = \Omega_0^2 \quad [A-13]$$

and

$$\beta_0 = \beta_1 = \frac{kT}{M_1 D_1} \quad [A-14]$$

The low frequency constant, Ω_0^2 , is usually equal to zero for a freely diffusing particle (6), however, in our case, this frequency is nonzero since the solvent particles of interest are interacting strongly with both the electrode surface and the desorbing particle and hence, are not freely diffusing.

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