University of Washington
Department of Chemistry
Chemistry 553
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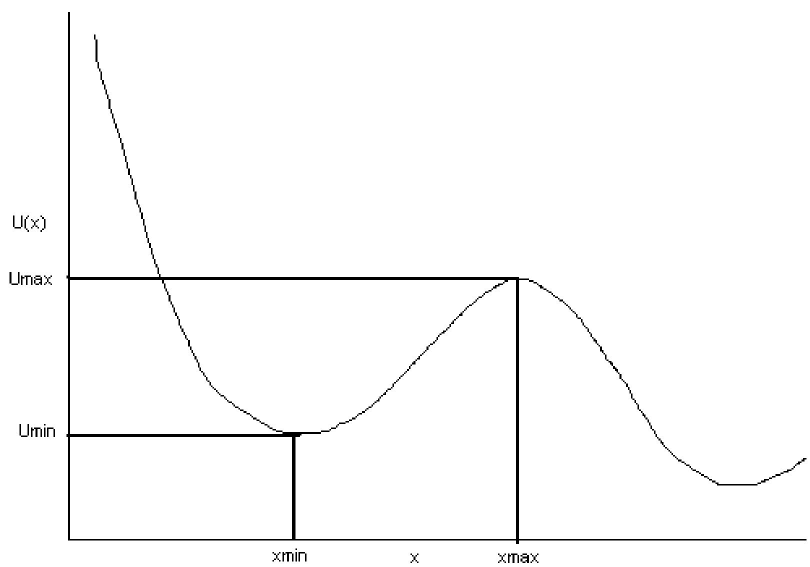
Lecture 15: Diffusion of Particles over Barriers:
04/29/11

A. Diffusion over Barriers: High Damping Limit

- Suppose a Brownian particle encounters a barrier in the course of its movements. We have shown that the effect of an external potential U(x) is easily incorporated into the FPE, but considerable simplification for barrier crossing is possible if we consider behavior for times $t \gg \tau = mB$. Then the behavior of the particle can be treated according to the Smoluchowski equation…

$$\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial x^2} + B\frac{\partial}{\partial x}\left(U'(x)W\right) \tag{15.1}$$

- In addition to taking the steady-state limit, we make the following assumptions…
    i. All B-particles start in the left hand well, and the distribution about x_{min} is assumed to be of stationary form.
    ii. Because no particles exist to the right of the barrier, a B-particle current flows from left to right.
    iii. We assume the barrier height is large compared to thermal activations so $Q = U_{\max} - U_{\min} >> kT$. We assume the stationary current is very small



- Recall Fick's First Law

$$\frac{\partial W}{\partial t} = -\frac{\partial J}{\partial x} \quad (15.2)$$

where J is the flux or current.

- In the stationary limit (15.1) is

$$\frac{\partial W}{\partial t} = -\frac{\partial J}{\partial x} = 0 = D\frac{\partial^2 W}{\partial x^2} + B\frac{\partial}{\partial x}\left(U'(x)W\right) \quad (15.3)$$

- Integrate (15.2)

$$J_{st} = -D\frac{\partial W_{st}}{\partial x} - BU'(x)W_{st} \quad (15.4)$$

where J_s is the stationary current.

- If the stationary current is small then (15.4) has the solution

$$W_{st}(x) = Ne^{-U(x)/k_BT} \quad (15.5)$$

- To determine N, expand U(x) in a Taylor series around $x=x_{min}$

$$U(x) = U_{\min} + \left(\frac{\partial^2 U}{\partial x^2}\right)_{x_{\min}} \frac{(x-x_{\min})^2}{2} + \ldots \approx U_{\min} + m\omega_{\min}^2 \frac{(x-x_{\min})^2}{2} \quad (15.6)$$

- Then

$$N = W_{st}(x_{\min})e^{U_{\min}/k_BT}$$

- Equation (15.5) becomes

$$W_{st}(x) = W_{st}(x_{\min})e^{-m\omega_{\min}^2(x-x_{\min})^2/2k_BT} \quad (15.7)$$

- Now to obtain the expression for the stationary B-particle current corresponding to the transfer of particles from $x_{min}=x_A$ to some point x_C that lies well to the right of the barrier maximum ($x_{max}=x_B$), use the identity

$$J_{st} = -D\exp\left\{-\frac{U(x)}{kT}\right\}\frac{\partial}{\partial x}\left(W_{st}(x)\exp\left\{\frac{U(x)}{kT}\right\}\right) \quad (15.8)$$

- We integrate both sides of (15.8) from x_A "A" to x_C "C"…

$$\begin{aligned} J_{st}\int_A^C \exp\left\{\frac{U(x)}{kT}\right\}dx &= -D\int_A^C \frac{\partial}{\partial x}\left(W_{st}(x)\exp\left\{\frac{U(x)}{kT}\right\}\right)dx \\ &= DW_{st}(x)\exp\left\{\frac{U(x)}{kT}\right\}\Bigg|_C^A \end{aligned} \quad (15.9)$$

- The expression for the stationary particle current is

$$J_{st} = D\frac{W_{st}(x_A)\exp\left\{\frac{U(x_A)}{kT}\right\} - W_{st}(x_C)\exp\left\{\frac{U(x_C)}{kT}\right\}}{\int_A^C \exp\left\{\frac{U(x)}{kT}\right\}dx} \approx D\frac{W_{st}(x_A)\exp\left\{\frac{U_{\min}}{kT}\right\}}{\int_A^C \exp\left\{\frac{U(x)}{kT}\right\}dx} \quad (15.10)$$

where the final expression in (15.10) follows because $W_{st}\left(x_C\right)\approx 0$

- Now the Kramers escape rate R_K is defined as the stationary current divided by the number of particles in the well

$$R_K=\frac{J_{st}}{N_{well}} \tag{15.11}$$

- Assuming the distribution in the well is given by (15.7) the population in the well follows from the integration

$$\begin{aligned}N_{well}&=\int_{x_1}^{x_2}W_{st}\left(x\right)dx\approx W_{st}\left(x_A\right)\int_{-\infty}^{+\infty}dxe^{-m\omega_A^2\left(x-x_A\right)^2/2k_BT}\\&=\frac{W_{st}\left(x_A\right)}{\omega_A}\left(\frac{2\pi k_BT}{m}\right)^{1/2}\end{aligned} \tag{15.12}$$

- Dividing (15.10) by (15.12) we obtain for (15.11)

$$R_K=\frac{J_{st}}{N_{well}}\approx D\omega_A\sqrt{\frac{m}{2\pi kT}}e^{U_{\min}/k_BT}\left\{\int_A^C\exp\left\{\frac{U\left(x\right)}{kT}\right\}dx\right\}^{-1} \tag{15.13}$$

- The integral $\int_A^C\exp\left\{\frac{U\left(x\right)}{kT}\right\}dx$ is evaluated in the following way. We are concerned mainly with the value of the per particle current at the barrier maximum, i.e. near $x_B=x_{max}$…where the potential is

$$U\left(x\right)=U\left(x_B\right)-\left(\frac{\partial^2U}{\partial x^2}\right)_{x=x_B}\frac{\left(x-x_B\right)^2}{2}+\ldots\approx U_{\max}-\frac{m\omega_B^2\left(x-x_B\right)^2}{2} \tag{15.14}$$

- We can now evaluate the integral in (15.3) as

$$\begin{aligned}\int_A^C\exp\left\{\frac{U\left(x\right)}{kT}\right\}dx&\approx e^{U_{\max}/kT}\int_{-\infty}^{\infty}\exp\left\{-\frac{m\omega_B^2x^2}{2kT}\right\}dx\\&=e^{U_{\max}/kT}\sqrt{\frac{2\pi kT}{m\omega_B^2}}\end{aligned} \tag{15.15}$$

- The final expression for the escape rate is

$$\begin{aligned}R_K&=\frac{J_{st}}{N_{well}}=D\omega_A\sqrt{\frac{m}{2\pi kT}}e^{U_{\min}/kT}\left\{e^{U_{\max}/kT}\sqrt{\frac{2\pi kT}{m\omega_B^2}}\right\}^{-1}\\&=De^{-Q/kT}\left(\frac{m\omega_A\omega_B}{2\pi kT}\right)=m\omega_A\omega_B\frac{Be^{-Q/kT}}{2\pi}=\left(\left(\frac{\partial^2U}{\partial x^2}\right)_{x=x_A}\left|\left(\frac{\partial^2U}{\partial x^2}\right)_{x=x_B}\right|\right)^{1/2}\frac{Be^{-Q/kT}}{2\pi}\end{aligned} \tag{15.16}$$

where $Q=U_{\max}-U_{\min}$