IP326. Lecture 26. Tuesday, April 2, 2019

● Kramers' reaction rate theory (cont.'d).

As discussed previously, Kramers' theory of chemical reactions is based on a model in which a chemical reaction is assumed to take place when a Brownian particle in one dimension passes randomly from a potential well on one side of a barrier to a potential well on the other side. The rate constant for this barrier-crossing event is the quantity of interest in the theory, being identified with the rate constant of the chemical reaction itself. It is expressed as the ratio of the steady-state probability current across the top of the barrier to the steady-state particle population in the reactant well. We've shown that these steady-state probabilities are obtained from the solution of the following equation:

$$-v\frac{\partial P}{\partial x}+\frac{\zeta}{m}\frac{\partial}{\partial v}vP+\frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial P}{\partial v}+\frac{\zeta k_B T}{m^2}\frac{\partial^2 P}{\partial v^2}=0 \qquad (1)$$

We've also shown that one such solution is just the equilibrium Boltzmann distribution, viz.,

$$P_0(x,v)=C\exp\left[-\beta m v^2/2-\beta U\right] \qquad (2)$$

where $\beta=1/k_B T$.

Kramers argued that this solution would not hold at the barrier top, since the particle would be in unstable equilibrium there. But he assumed that the system could nevertheless exist in a steady state, and that the phase space density at the barrier, $P_B(x,v)$, could therefore be written in the form

$$P_B(x,v)=P_0(x,v)G(x,v) \qquad (3)$$

where $G(x,v)$ is an unknown function to be determined. We turn to a determination of this function next.

As a first step we substitute the above expression into the LHS of Eq. (1). The result is

$$-v\left(\frac{\partial G}{\partial x}P_0+G\frac{\partial P_0}{\partial x}\right)+\frac{\zeta}{m}\left(G\frac{\partial vP_0}{\partial v}+vP_0\frac{\partial G}{\partial v}\right)+\frac{1}{m}\frac{\partial U}{\partial x}\left(G\frac{\partial P_0}{\partial v}+P_0\frac{\partial G}{\partial v}\right)+$$

$$+\frac{\zeta k_B T}{m^2}\left(2\frac{\partial G}{\partial v}\frac{\partial P_0}{\partial v}+G\frac{\partial^2 P}{\partial v^2}+\frac{\partial^2 G}{\partial v^2}\right)$$

$$= G\left[-v\frac{\partial P_0}{\partial x} + \frac{\zeta}{m}\frac{\partial}{\partial v}vP_0 + \frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial P_0}{\partial v} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 P_0}{\partial v^2} \right] + P_0\left[-v\frac{\partial G}{\partial x} + \frac{\zeta}{m}v\frac{\partial G}{\partial v} + \right.$$

$$\left. + \frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial G}{\partial v} + \frac{2\zeta k_B T}{m^2}\frac{\partial G}{\partial v}\frac{(-mv)}{k_B T} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial v^2} \right] \tag{4}$$

Because P_0 satisfies Eq. (1), the contribution from the terms in the first set of square brackets in Eq. (4) vanishes. At the same time, if Eq. (3) is truly to be a solution of Eq. (1) , then the contribution from the terms in the second set of square brackets must vanish too. In other words, the function *G* must satisfy the equation

$$\left[-v\frac{\partial G}{\partial x} - \frac{\zeta}{m}v\frac{\partial G}{\partial v} + \frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial G}{\partial v} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial v^2} \right] = 0 \tag{5}$$

Kramers next assumed that near the barrier top the potential U could be approximated as inverted parabola, that is, as

$$U(x) \approx E_B - \frac{m\omega_B^2}{2}(x - x_B)^2 \tag{6}$$

where E_B is the height of the barrier, ω_B is a frequency (reflecting the curvature at the barrier top), and x_B is the location of the barrier maximum. Given this approximation for *U*, it follows that

$$\frac{\partial U(x)}{\partial x} \approx -m\omega_B^2(x - x_B) \tag{7}$$

and when this expression is substituted into Eq. (5), the result is

$$\left[v\frac{\partial G}{\partial x} + \left(\frac{\zeta}{m}v + \omega_B^2(x - x_B) \right)\frac{\partial G}{\partial v} - \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial v^2} \right] = 0 \tag{8}$$

In general, there is no systematic procedure for finding the solution to partial differential equations, but it's possible to guess a solution, and in the case of Eq. (8), one solution that will satisfy it is $G(x) = \text{constant}$, but this would imply that the steady-state solution at the barrier top, $P_B(x, v)$, is just the equilibrium Boltzmann distribution, which as argued is not expected to hold when the system is in unstable equilibrium. So the solution $G(x) = \text{constant}$ is not relevant. Kramer then suggested that another solution might be one where *G* is a function not of *x* and *v* separately but of a linear combination of the two. That is,

$$G(x, v) = G(u) \tag{9a}$$

where

$$u = v - \lambda(x - x_B) \tag{9b}$$

with λ an unknown parameter that is also to be determined. If G has this suggested structure then Eq. (8) must now be rewritten in terms of the new variable u. This is accomplished by noting that

$$\frac{\partial}{\partial v} = \frac{\partial u}{\partial v}\frac{\partial}{\partial u} = \frac{\partial}{\partial u}, \qquad \frac{\partial^2}{\partial v^2} = \frac{\partial}{\partial u^2}, \quad \text{and} \quad \frac{\partial}{\partial x} = \frac{\partial u}{\partial x}\frac{\partial}{\partial u} = -\lambda\frac{\partial}{\partial u}$$

Using these relations in Eq. (8), we find that

$$\left[\left(-\lambda v + \frac{\zeta}{m}v + \omega_B^2(x - x_B)\right)\frac{\partial G}{\partial u} - \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial u^2}\right] = 0,$$

which, after collecting terms and rearranging, becomes

$$\left[\left(\left\{\lambda - \frac{\zeta}{m}\right\}v - \omega_B^2(x - x_B)\right)\frac{\partial G}{\partial u} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial u^2}\right] = 0 \tag{10}$$

The only way this equation can be a function solely of the variable u is if the following condition is satisfied:

$$\left(\lambda - \frac{\zeta}{m}\right)v - \omega_B^2(x - x_B) = \mu u \tag{11}$$

where μ is another unknown to-be-determined parameter. If v in this condition is now replaced by its expression in terms of u and x in Eq. (9b), Eq. (11) becomes

$$\left(\lambda - \frac{\zeta}{m}\right)[u + \lambda(x - x_B)] - \omega_B^2(x - x_B) = \mu u$$

which can be rearranged to

$$\left(\lambda - \frac{\zeta}{m}\right)u + \left[\lambda\left(\lambda - \frac{\zeta}{m}\right) - \omega_B^2\right](x - x_B) = \mu u \tag{12}$$

One way to make both sides of this equation equal is to require that

$$\mu = \lambda - \frac{\zeta}{m} \tag{13a}$$

and

$$\lambda^2 - \lambda \frac{\zeta}{m} - \omega_B^2 = 0 \tag{13b}$$

The second of these conditions determines λ, and once λ is determined, the first equation determines μ. Equation (13b) is, of course, satisfied by

$$\lambda = \frac{1}{2}\left[\frac{\zeta}{m} \pm \sqrt{\frac{\zeta^2}{m^2} + 4\omega_B^2}\right]$$

$$= \frac{\zeta}{2m} \pm \sqrt{\frac{\zeta^2}{4m^2} + \omega_B^2} \tag{14}$$

Substituting Eq. (11) in Eq. (10), and using Eq. (13a) for the parameter μ, we now find that the function G must satisfy the equation

$$\left[\left(\lambda - \frac{\zeta}{m}\right) u \frac{\partial G}{\partial u} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 G}{\partial u^2}\right] = 0 \tag{15}$$

which is solved by

$$G(u) = N \int_{-\infty}^{u} dz \exp\left[-\frac{m^2}{2\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) z^2\right] \tag{16}$$

where N is a normalization constant. One can confirm that Eq. (16) solves Eq. (15) by direct substitution, noting that

$$\frac{\partial G(u)}{\partial u} = N \exp\left[-\frac{m^2}{2\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) u^2\right]$$

$$\frac{\partial^2 G(u)}{\partial u^2} = -N \frac{m^2}{\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) u \exp\left[-\frac{m^2}{2\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) u^2\right]$$

Therefore,

$$\left(\lambda - \frac{\zeta}{m}\right) u \frac{\partial G}{\partial u} + \frac{\zeta k_B T}{m^2} \frac{\partial^2 G}{\partial u^2} = N \exp\left[-\frac{m^2}{2\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) u^2 \right] \left[\left(\lambda - \frac{\zeta}{m}\right) u + \right.$$

$$\left. + \frac{\zeta k_B T}{m^2} \frac{(-m^2)}{\zeta k_B T} \left(\lambda - \frac{\zeta}{m}\right) u \right]$$

$$= 0$$

From the structure of Eq. (16), it's clear that in order for the coefficient of z^2 in the argument of the exponential to be negative (which it should be for the function $G(u)$ to be well-behaved), the positive root must be selected for λ in Eq. (14). In other words,

$$\lambda = \frac{\zeta}{2m} + \sqrt{\frac{\zeta^2}{4m^2} + \omega_B^2} \tag{17}$$

Furthermore, the normalization constant in Eq. (16) can be determined by requiring that when x is large and negative (meaning the system is in the reactant well, on the left side of the barrier), the phase space distribution $P_B(x,v)$ should recover the equilibrium thermal distribution $P_0(x,v)$. From the definition of $P_B(x,v)$, (see Eq. (3)), this in turn requires that $G(x,v)$ be unity. Since large negative x corresponds to large positive u (see Eq. (9b)), this requirement becomes

$$N \int_{-\infty}^{\infty} dz \exp\left[-\frac{m^2}{2\zeta k_B T}\left(\lambda - \frac{\zeta}{m}\right) z^2 \right] = 1 \tag{18}$$

which fixes N as

$$N = \sqrt{\frac{m^2(\lambda - \zeta/m)}{2\pi\zeta k_B T}} \tag{19}$$

We're now finally in a position to calculate the flux and population, the quantities we need to derive an expression for the rate constant k.

Recall that the steady-state flux of probability over the barrier was defined in terms of the mean particle velocity in the neighbourhood of the barrier in the $t \to \infty$ limit. In other words

$$\text{Flux} \equiv J_B(x,v,t\to\infty) = \int_{-\infty}^{\infty} dv\, v\, P(x = x_B, v, t \to \infty)$$

$$= Ce^{-E_B}\int_{-\infty}^{\infty} dv\, v\, e^{-\beta m v^2/2} G(v)$$

$$= CNe^{-\beta E_B}\int_{-\infty}^{\infty} dv\, v\, e^{-\beta m v^2/2}\int_{-\infty}^{v} dz \exp\left[-\Omega z^2/2\right] \tag{20}$$

where $\Omega \equiv (\lambda - \zeta/m)m^2/\zeta k_B T$. Equation (20) can be evaluated by first rewriting it as

$$J_B = -\frac{CN}{\beta m} e^{-\beta E_B}\int_{-\infty}^{\infty} dv \left(\frac{\partial e^{-\beta m v^2/2}}{\partial v}\right)\int_{-\infty}^{v} dz \exp\left[-\Omega z^2/2\right]$$

and then integrating by parts, which yields

$$J_B = -\frac{CN}{\beta m} e^{-\beta E_B}\left[e^{-\beta m v^2/2}\int_{-\infty}^{v} dz e^{-\Omega z^2/2}\Bigg|_{v=-\infty}^{v=\infty} - \int_{-\infty}^{\infty} dv e^{-\beta m v^2/2} e^{-\Omega v^2/2}\right]$$

$$= \frac{CN}{\beta m} e^{-\beta E_B}\sqrt{\frac{2\pi}{\beta m + \Omega}} \tag{21}$$

The factor of $\beta m + \Omega$ in the last expression simplifies to

$$\beta m + \Omega = \beta m + \frac{\lambda m^2}{\zeta k_B T} - \frac{m}{k_B T} = \frac{\lambda m^2}{\zeta k_B T}$$

So, finally,

$$J_B = CN\frac{k_B T}{m^2} e^{-\beta E_B}\sqrt{\frac{2\pi \zeta k_B T}{\lambda}} \tag{22}$$

Recall also that we had defined the population in the reactant well, N_A, as

$$\text{Population} \equiv N_A = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv P_0(x, v)$$

Assuming that the potential energy U of the system in this region can be approximated by $U = E_0 + (m\omega_0^2/2)(x - x_0)^2$, where E_0 is the height of the reactant well at the location of the minimum x_0, and ω_0 is a frequency, which is related to the well's curvature, we can write N_A as

$$N_A = Ce^{-\beta E_0} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv e^{-\beta m v^2/2} e^{-\beta m \omega_0^2 (x-x_0)^2/2} \tag{23}$$

Evaluating the integrals in (23), we arrive at

$$N_A = Ce^{-\beta E_0} \frac{2\pi k_B T}{m\omega_0} \tag{24}$$

Taking the ratio of Eqs. (22) and (24), we obtain the following expression for the rate constant k:

$$k = Ne^{-\beta(E_B - E_0)} \frac{\omega_0}{m} \sqrt{\frac{\zeta k_B T}{2\pi\lambda}} \, ,$$

which, after the substitution of the definition of N (see Eq. (19)), becomes

$$k = e^{-\beta(E_B - E_0)} \frac{\omega_0}{2\pi} \sqrt{\frac{(\lambda - \zeta/m)}{\lambda}} \tag{25}$$

The parameter λ in this relation should now be replaced by its expression from Eq. (17); when this is done the factor $\sqrt{(\lambda - \zeta/m)/\lambda}$ becomes

$$\begin{aligned}
\sqrt{\frac{(\lambda - \zeta/m)}{\lambda}} &= \sqrt{\frac{\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2} - \zeta/m}{\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}} \\
&= \sqrt{\frac{-\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}{\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}} \\
&= \sqrt{\frac{-\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}{\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}} \times \frac{\sqrt{-\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}}{\sqrt{-\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}} \\
&= \frac{-\zeta/2m + \sqrt{\zeta^2/4m^2 + \omega_B^2}}{\sqrt{-\zeta^2/4m^2 + \zeta^2/4m^2 + \omega_B^2}} \\
&= \frac{1}{\omega_b}\left(\sqrt{\frac{\zeta^2}{4m^2} + \omega_B^2} - \frac{\zeta}{2m}\right)
\end{aligned} \tag{26}$$

Therefore,

$$k = \frac{\omega_0}{2\pi\omega_B}\left(\sqrt{\frac{\zeta^2}{4m^2}+\omega_B^2}-\frac{\zeta}{2m}\right)e^{-\beta(E_B-E_0)} \tag{27}$$

This is the final expression for the rate constant, but it's instructive to consider it in different limits. For instance, suppose $\zeta/2m >> \omega_B$, which can be considered a high friction limit. To apply this limit to Eq. (27), rewrite it first as

$$k = \frac{\omega_0}{2\pi\omega_B}\left(\frac{\zeta}{2m}\sqrt{1+\frac{4m^2\omega_B^2}{\zeta^2}}-\frac{\zeta}{2m}\right)e^{-\beta(E_B-E_0)}$$

and then expand the radical to lowest non-trivial order:

$$k = \frac{\omega_0}{2\pi\omega_B}\left(\frac{\zeta}{2m}\left[1+\frac{2m^2\omega_B^2}{\zeta^2}+\cdots\right]-\frac{\zeta}{2m}\right)e^{-\beta(E_B-E_0)}$$

$$= \frac{m\omega_0\omega_B}{2\pi\zeta}e^{-\beta(E_B-E_0)} \tag{28}$$

In the opposite limit, viz., $\zeta/2m << \omega_B$, Eq. (27) immediately simplifies to

$$k = \frac{\omega_0}{2\pi}e^{-\beta(E_B-E_0)} \tag{29}$$

This is the expression that is generally referred to as the <u>transition theory</u> rate, which postulates that the rate constant is proportional to two factors, one related to the energy barrier, and the other to the frequency (ω_0) with which the reactants come together. Equation (28) incorporates an additional friction dependence, which reflects the nature of the bath, as well as a second frequency dependence associated with the curvature at the top of the barrier.