EQUATIONS AND RELATIONSHIPS
FROM VARIOUS THEORIES OF REACTION RATES

I. TRANSITION STATE THEORY (Eyring, 1935)

Fowler and Guggenheim (1952): Eqn. (1208.7) for a bimolecular reaction,

$$k_2 = \kappa \frac{\phi_T(T)}{\phi_1(T)\phi_2(T)} \frac{kT}{h} e^{-\varepsilon_0/kT} \tag{I.1}$$

Hynes (1988): Eqn. (2) for an isomerization,

$$k^{TST} = \frac{kT}{h} \frac{Q^{\ddagger}}{Q_R} e^{-\Delta E^{\ddagger}/k_B T} \tag{I.2}$$

Hynes (1988): Eqn. (4) for an isomerization,

$$k^{TST} = \frac{\omega_R}{2\pi} e^{-\Delta G^{\ddagger}/k_B T} \tag{I.3}$$

where ω_R is the vibrational frequency along the reaction coordinate for the reactant well.

TST was known to give a high estimate for a reaction rate. The true rate of reaction was smaller by a factor κ:

$$k = \kappa \, k^{TST} \tag{I.4}$$

The factor κ could not be calculated by TST. It has been the object of many other theoretical treatments.

II. KRAMERS THEORY (Kramers, 1940)

Hynes (1988): Eqn. (9) for Kramers calculation of the factor κ, for the strong coupling regime,

$$\kappa^{Kramers} = [1 + \alpha^2]^{1/2} - \alpha \qquad \text{(II.1)}$$

$$\alpha = \frac{\zeta}{2\omega_b}$$

where ζ is the solvent viscosity, and ω_b is the frequency corresponding to the curvature of the reaction coordinate at the top of the barrier, analogous to ω_R which corresponds to the curvature of the reactant well bottom. The time of passage over the barrier top (time spent near the barrier top) is inversely proportional to ω_b.

For limiting high viscosity, $\zeta >> 2\omega_b$,

$$\kappa^{Kramers,overdamped} = \frac{\omega_b}{\zeta} \qquad \text{(II.2)}$$

and the reaction rate for a two-well potential is

$$k^{Kramers,overdamped} = \frac{\omega_b}{\zeta}\frac{\omega_R}{2\pi}e^{-\Delta G^{\ddagger}/k_B T} \qquad \text{(II.3)}$$

For low viscosity, $\zeta < 2\omega_b$, $\kappa^{Kramers} = 1$ and the TST estimate of the reaction rate is correct, i.e., the low viscosity limit of Kramers theory (for the high coupling regime) is the TST rate.

III. REACTIVE FLUX (Chandler, 1978)

Chandler (1998): Eqn. (16-17 = 6.1-6.2) for the reactive flux,

$$k(t) = -\frac{d}{dt}C_{\delta h} = -\frac{d}{dt}\frac{<\delta h \delta h(t)>}{<(\delta h)^2>} \tag{III.1a}$$

$$= \frac{1}{x\,(1-x)}<\dot{q}\;\delta(q-q^*)\;h(q(t))> \tag{III.1b}$$

$$= \frac{1}{x\,(1-x)}P(q^*)<\dot{q}\;h(q(t))>_{q^*} \tag{III.2}$$

Chandler (1998): Eqn. (18 = 6.3) for the TST rate,

$$k^{TST} = k(0^+) = \frac{1}{x\,(1-x)}P(q^*)<\dot{q}\;\theta(\dot{q})>_{q^*} \tag{III.3}$$

which for a symmetrical two-well potential evaluates as

$$k^{TST}_{A\rightarrow B} = \frac{1}{2}<|\dot{q}|>_{q^*}\frac{e^{-\Delta W^*/kT}}{Q} \tag{III.4}$$

$$= \frac{\omega_A}{2\pi}e^{-\Delta W^*/kT} \tag{III.5}$$

Eqn. (III.5) is identical with Eqn. (I.3).

Chandler (1998): Eqn. (21 = 6.6) for κ,

$$\kappa = \frac{k}{k^{TST}} = \frac{k(t^*)}{k(0^+)} \tag{III.6}$$

where the time t^* is in the range $\tau_{mol} < t^* << \tau_{rxn} = 1/k$; τ_{mol} is the characteristic time of transient processes at the barrier top.

IV. OTHER THEORETICAL TREATMENTS OF RATES OF REACTION IN SOLUTION

A. Grote-Hynes theory (1980): treats the case of high, sharp barriers, for which, owing to short residence time at the top of the barrier, the simple Langevin description with constant friction fails, and thus Kramers theory fails also. Grote-Hynes theory for solution reactions is based on the Generalized Langevin equation, with memory friction.

B. Multidimensional transition state theory: treats a multidimensional reaction coordinate. This can be complicated coupling between the reaction coordinate and other degrees of freedom, such as solvent, as treated by Grote-Hynes and Kramers theories. It has been shown that Multidimensional transition state theory and Grote-Hynes theory are equivalent expressions of the same underlying model. Kramers theory and TST theory are limiting cases of each.

C. Lowest eigenvalue for the dynamical equation governing evolution of the coarse-grained probability density, e.g., equations of the Fokker-Planck type.

D. Mean-first-passage time: another approach to solution of stochastic dynamical equations.