

Lecture 1: Chemical Reaction Rate Theory

Starting from time-dependent perturbation theory and the Fluctuation Dissipation Theorem, we are ready to apply the theorem to develop a microscopic theory of chemical reaction rates. The following is based on the presentation of Chandler, Chap. 8, but from a quantum mechanical perspective.

A. Phenomenological rate expressions

We consider the unimolecular reactions of the form



where k_{BA} and k_{AB} are the forward and reverse rate constants, respectively.

The differential form of the rate law for this reaction is

$$\frac{d}{dt}c_A(t) = -k_{BA}c_A(t) + k_{AB}c_B(t) \quad (2)$$

where c_A and c_B indicate the concentration of the two species. The integrated form of this rate law is

$$\Delta c_A(t) = c_A(t) - c_A^{(\text{eq})} = \Delta c_A(0)e^{-t/\tau} \quad (3)$$

where $c_A^{(\text{eq})}$ is the equilibrium expectation value for the concentration and $\tau^{-1} = k_{AB} + k_{BA}$.

B. Connecting to microscopic quantities

We introduce a quantity that reports on the (time-dependent) probability with which the system is to be found in the reactant region, such that

$$\langle n_A(t) \rangle \propto c_A(t). \quad (4)$$

The specific form of n_A will be discussed shortly. Note that, as in previous lectures, the notation for the LHS indicates an expectation value with respect to the time-dependent density matrix of the system. Defining $\Delta n_A(t) = \langle n_A(t) \rangle - \langle n_A \rangle_0$ and $\delta n_A = n_A - \langle n_A \rangle_0$, where $\langle \cdot \rangle_0$ indicates the expectation value with respect to the equilibrium density matrix, ρ_0 , we have

$$\frac{\Delta c_A(t)}{\Delta c_A(0)} = \frac{\Delta n_A(t)}{\Delta n_A(0)} \quad (5)$$

Then, recognizing that the expression on the RHS is simply the relaxation of a system from an initially prepared non-equilibrium state, we can directly apply the Fluctuation Dissipation Theorem (in the form of Onsager's Regression Hypothesis) to express the dynamics of the relaxation in terms of an equilibrium Kubo-transform time correlation function,

$$\frac{\Delta c_A(t)}{\Delta c_A(0)} = \frac{\tilde{C}_{\delta n_A \delta n_A}(t)}{\tilde{C}_{\delta n_A \delta n_A}(0)} \quad (6)$$

Finally, combining this relation with Eq. 3 yields

$$e^{-t/\tau} = \frac{\tilde{C}_{\delta n_A \delta n_A}(t)}{\tilde{C}_{\delta n_A \delta n_A}(0)} \quad (7)$$

This is an important and remarkable result, fully expressing the phenomenological rate constant (on the LHS) to the underlying microscopic dynamics of the system.

Given that n_A is a quantity that characterizes whether the system is in either the reactant or product region, we can relate it to a Heaviside function of position

$$n_A = h_A[q(\mathbf{r})] = \begin{cases} 1, & q(\mathbf{r}) < q^* \\ 0, & q(\mathbf{r}) > q^* \end{cases} \quad (8)$$

where $q(\mathbf{r})$ is a position-dependent reaction coordinate, and q^* describes the "dividing surface" along that reaction coordinate that divides reactant from product. For simplicity, we shall assume that $q(\mathbf{r})$ is a linear function of position, but this need not be the case in general. (See picture.) Note that we can likewise define a characteristic function that reports whether the system is on the product side, $h_B[q(\mathbf{r})] = 1 - h_A[q(\mathbf{r})]$.

We can thus write the numerator in Eq. 7 in a more explicit manner

$$\tilde{C}_{\delta n_A \delta n_A}(t) = \text{Tr}\{\rho_0(\tilde{h}_A(0) - \langle \tilde{h}_A \rangle_0)(h_A(t) - \langle h_A \rangle_0)\} \quad (9)$$

$$= \tilde{C}_{h_A h_A}(t) + \langle h_A \rangle_0^2 - \text{Tr}\{\rho_0 \tilde{h}_A\} \langle h_A \rangle_0 - \langle h_A \rangle_0 \text{Tr}\{\rho_0 e^{iHt/\hbar} h_A e^{-iHt/\hbar}\} \quad (10)$$

$$= \tilde{C}_{h_A h_A}(t) - x_A^2 \quad (11)$$

where the last equality uses that the dynamics of the system Hamiltonian H preserves the equilibrium density matrix, and $\langle h_A \rangle_0 = \langle \tilde{h}_A \rangle_0 \equiv x_A$.

Similarly, we can manipulate the denominator in Eq. 7 as follows

$$\tilde{C}_{\delta n_A \delta n_A}(0) = \tilde{C}_{h_A h_A}(0) - x_A^2 \quad (12)$$

$$= \text{Tr}\{\rho_0 \tilde{h}_A h_A\} - x_A^2 \quad (13)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{-(\beta-\lambda)H} h_A e^{-\lambda H} h_A \right\} - x_A^2 \quad (14)$$

$$\approx \frac{1}{Q} \text{Tr} \left\{ e^{-\beta H} h_A h_A \right\} - x_A^2 \quad (15)$$

$$= \frac{1}{Q} \text{Tr} \left\{ e^{-\beta H} h_A \right\} - x_A^2 \quad (16)$$

$$= x_A - x_A^2 = x_A(1 - x_A) = x_A x_B, \quad (17)$$

where $x_B \equiv \langle h_B \rangle_0$. The only non-trivial step in this manipulation is the approximation to arrive at Eq. 15, by assuming that $[H, h_A] = 0$. Assuming that the equilibrium probability density for the reactant is located in region of space that are not overlapping with the dividing surface defined by q^* , then h_A is simply a constant that trivially commutes with any operator; for the case in which a phenomenological rate constant actually exists (i.e., there is a sufficiently high reaction barrier that there is a separation of timescales between equilibration in the reactant region and crossing the barrier to the product) then this assumption is an excellent one, introducing essentially no error.

Finally, combining the results from Eqs. 17 and 11 with Eq. 7, we have

$$\tilde{C}_{h_A h_A}(t) = x_A^2 + x_A x_B e^{-t/\tau}. \quad (18)$$

This wonderful result again relates the rate constant in terms of the microscopic dynamics of the system, as expressed by the Kubo-transformed TCF. Moreover, it suggests a practical strategy for obtaining the reaction rate: Simply time-evolve the dynamics monitor decay of the TCF to extract the rate constant. This strategy is useful for cases in which the barrier for the reaction is pretty low, but what is the problem when there is a high barrier for the reaction? Answer: The TCF must be evolved for exponentially long timescales to see any of the barrier-crossing dynamics. Ouch!

C. The Flux-Side form of the Rate Constant

To arrive at another very useful form of the rate constant, consider the derivative of Eq. 18,

$$\frac{d}{dt} \tilde{C}_{h_A h_A}(t) = -\frac{x_A x_B}{\tau} e^{-t/\tau} \quad (19)$$

Before proceeding, we briefly derive the statement of time-reversibility for Kubo-transformed TCFs, considering general operators A and B :

$$\tilde{C}_{AB}(t) = \text{Tr}\{\rho_0 \tilde{A}(0) B(t)\} \quad (20)$$

$$= \text{Tr}\{\rho_0 \tilde{A}(-t) B(0)\} \quad (\text{time-translational symmetry; time-invariance of } \rho_0) \quad (21)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{iH(-t)/\hbar} A e^{-iH(-t)/\hbar} e^{-\lambda H} B e^{-(\beta-\lambda)H} \right\} \quad (\text{cyclic permutation}) \quad (22)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{-\lambda H} B e^{-(\beta-\lambda)H} e^{iH(-t)/\hbar} A e^{-iH(-t)/\hbar} \right\} \quad (\text{cyclic permutation}) \quad (23)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{-(\beta-\lambda)H} B e^{-\lambda H} e^{iH(-t)/\hbar} A e^{-iH(-t)/\hbar} \right\} \quad (\text{change int. vars.}) \quad (24)$$

$$= \text{Tr}\{\rho_0 \tilde{B}(0) A(-t)\} \quad (25)$$

$$\tilde{C}_{AB}(t) = \tilde{C}_{BA}(-t) \quad (26)$$

This statement of time reversibility clearly shows that Kubo-transformed autocorrelation functions (for which $A = B$) are even functions of time. Differentiating the result with respect to time yields

$$\frac{d}{dt} \tilde{C}_{AB}(t) = -\frac{d}{dt} \tilde{C}_{BA}(-t) = -\tilde{C}_{B\dot{A}}(-t) \quad (27)$$

which shows that the time-derivative of Kubo-transformed autocorrelation functions are odd functions of time.

Applying this result to $\frac{d}{dt} \tilde{C}_{h_A h_A}(t)$ yields

$$\frac{d}{dt} \tilde{C}_{h_A h_A}(t) = -\tilde{C}_{h_A \dot{h}_A}(-t) \quad (28)$$

$$= -\text{Tr} \left\{ \rho_0 \tilde{h}_A e^{iH(-t)/\hbar} \dot{h}_A e^{-iH(-t)/\hbar} \right\} \quad (29)$$

$$= \text{Tr} \left\{ \rho_0 \tilde{h}_A e^{iH(-t)/\hbar} F e^{-iH(-t)/\hbar} \right\} \quad (30)$$

where $F \equiv \dot{h}_B = \frac{i}{\hbar} [H, h_B] = -\dot{h}_A$ is the flux operator, which describes the reactive flux across the

dividing surface. Continuing,

$$\frac{d}{dt}\tilde{C}_{h_A h_A}(t) = \text{Tr} \left\{ \rho_0 \tilde{h}_A e^{iH(-t)/\hbar} F e^{-iH(-t)/\hbar} \right\} \quad (31)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{iHt/\hbar} h_A e^{-iHt/\hbar} e^{-\lambda H} F e^{-(\beta-\lambda)H} \right\} \quad (32)$$

$$= \frac{1}{\beta Q} \text{Tr} \left\{ \int_0^\beta d\lambda e^{-\lambda H} F e^{-(\beta-\lambda)H} e^{iHt/\hbar} h_A e^{-iHt/\hbar} \right\} \quad (33)$$

$$= \text{Tr} \left\{ \rho_0 \tilde{F}(0) h_A(t) \right\} \quad (34)$$

$$= \text{Tr} \left\{ \rho_0 \tilde{F}(0) (1 - h_B(t)) \right\} \quad (35)$$

$$= \text{Tr} \left\{ \rho_0 \tilde{F} \right\} - \text{Tr} \left\{ \rho_0 \tilde{F}(0) h_B(t) \right\} \quad (36)$$

$$= -\tilde{C}_{F h_B}(t) \quad (37)$$

where we have used that $\text{Tr} \left\{ \rho_0 \tilde{F} \right\}$ due to the fact that equilibrium distributions have no net flux through any surface. Finally, identifying $\tilde{C}_{F h_B}(t) \equiv \tilde{C}_{f_s}(t)$ as the “flux-side correlation function” that relates the *flux* of initial particle density with the probability of reaching the product *side* of the reaction, we can combine the last result with Eq. 19 to obtain

$$\tilde{C}_{f_s}(t) = \frac{x_A x_B}{\tau} e^{-t/\tau}. \quad (38)$$

D. Physical Interpretation, in the classical mechanical limit

For a classical mechanical system,

$$F(t) = \dot{h}_B(t) \quad (39)$$

$$= \dot{h}_B(q_t) \quad (40)$$

$$= \frac{d}{dt} \Theta(q_t - q^*) \quad (41)$$

$$= \delta(q_t - q^*) \dot{q}_t, \quad (42)$$

where q_t is the value of the reaction coordinate along the classical mechanical trajectory and $\Theta(x)$ is the standard Heaviside function. The flux-side correlation function then becomes

$$C_{f_s}^{(cl)}(t) = \langle \delta(q_0 - q^*) \dot{q}_0 h_B(q_t) \rangle_0, \quad (43)$$

such that trajectories are initialized from the dividing surface (pinned by the δ -function) and the initial velocity is correlated with the final side of the dividing surface that the trajectory reaches.

Discussion points, related to illustrative figures: (1) unreactive vs. reactive trajectories, (2) short-timescale: transient recrossing dynamics on the molecular timescale, t_{mol} , (3) intermediate timescale: plateau in the TCF once recrossing finishes and the trajectory “picks a side”, (4) very long times ($t \gg \tau = (k_{\text{AB}} + k_{\text{BA}})^{-1}$): the TCF decays to zero as the trajectory undergoes additional barrier-crossing events and becomes uncorrelated with the initial barrier crossing event.

Based on this discussion, to relate $\tilde{C}_{fs}(t)$ to the reaction rate, we consider the value of the TCF for times $t_{\text{mol}} \ll t \ll \tau$, which are long enough to reach the plateau value for the TCF after dynamical recrossing, but not so long such that additional barrier-crossing events start to occur. For this time range (indicated as $t \rightarrow “\infty”$), it follows that

$$e^{-t/\tau} \approx 1, \quad (44)$$

such that Eq. 38 becomes

$$\lim_{t \rightarrow “\infty”} \tilde{C}_{fs}(t) = \frac{x_{\text{A}} x_{\text{B}}}{\tau}. \quad (45)$$

Finally, by using the property of detailed balance,

$$\frac{x_{\text{B}}}{x_{\text{A}}} = \frac{k_{\text{BA}}}{k_{\text{AB}}}, \quad (46)$$

it is easy to show that $\tau^{-1} = \frac{k_{\text{BA}}}{x_{\text{B}}}$, such that Eq. 47 becomes

$$k_{\text{BA}} = \frac{1}{x_{\text{A}}} \lim_{t \rightarrow “\infty”} \tilde{C}_{fs}(t). \quad (47)$$

Subject to only very modest assumptions that are already necessary for the existence of a well-defined rate constant, this expression provides the exact quantum mechanical expression for the reaction rate in the flux-side formulation.