Raymond Kapral, Styliani Consta, and Liam McWhirter, *"Chemical rate laws and rate constants"*, in "Classical and Quantum Dynamics in Condensed Phase Simulations: proceedings of the International School of Physics, Lerici, Villa Marigola, 7 July-18 July 1997", B. J. Berne, G. Ciccotti, and D. F. Coker, eds., pp 583-616, World Scientific, Singapore, 1998.

"... for systems close to equilibrium where linearized versions of mass action laws apply, one may derive generalized forms of the rate laws from the microscopic evolution equations."

[The following is keyed to section headings and equation numbers in the Kapral et al. paper; the intent is to outline the logic of the development.]

2. - **Derivation of chemical rate laws.**

2.1 *Phenomenological description.* Define a progress variable,

$$\bar{\chi}(t) = (\nu_i - \bar{\nu}_i)^{-1}(\bar{N}_i(t) - \bar{N}_i^{eq}) \tag{6}$$

where $(\nu_i - \bar{\nu}_i)$ is the difference in stoichiometry, reactant - product, for chemical species *i*, and $(\bar{N}_i(t) - \bar{N}_i^{eq})$ is the difference from the equilibrium value of the average number of molecules for species *i* at time *t*.

For systems near equilibrium, the progress of the reaction, a return to equilibrium, is first order:

$$\frac{d\bar{\chi}(t)}{dt} = -k\bar{\chi}(t) \tag{7}$$

This expression is the phenomenological (macroscopic; experimental) rate law. The constant *k* is a relaxation rate constant. It can be expressed as a function of the forward and reverse step constants, with the form of the function depending on the particular chemical mechanism (see eq. 8 of Kapral et al. (1998)).

For example, for an isomerization reaction,

$$A \underset{k_r}{\overset{k_f}{\longleftrightarrow}} B \tag{9}$$

$$k = k_f + k_r$$

2.3 *Rate law derivation.* The derivation of a rate law from microscopic theory, for systems close to equilibrium, is done by use of the Mori-Zwanzig formalism. This method gives an *exact* description of the dynamics in the form of a Generalized Langevin equation for a particular set of (slow) variables of a system. Projection operators, P and $Q = I - P$, are used to separate the dynamics of $\hat{\chi}$ into a part that evolves in the subspace of phase space parallel with $\hat{\chi}$ and projected by P (more properly, this is a subspace of the Liouville space of all dynamical variables), and another part that evolves in a subspace orthogonal to $\hat{\chi}$, projected by Q and complementary to that projected by P. $\hat{\chi}$ is the only variable that evolves on the slow time scale of the chemical reaction, τ_{RXN}. Variables of the subspace defined by Q have fast dynamics; their dynamics are on the microscopic time scale, τ_{MIC}, of atomic collisions, bond stretching, etc.

From this analysis, the ensemble-averaged dynamics for the progress variable $\hat{\chi}$ is

$$\frac{d\overline{\chi}(t)}{dt} = -\int_0^t d\tau\ \tilde{k}(\tau)\,\overline{\chi}(t - \tau) \tag{24}$$

The dynamics of $\hat{\chi}$ can be expressed equivalently in terms of the time correlation function,

$$\frac{dC_\chi(t)}{dt} = -\int_0^t d\tau\ \tilde{k}(\tau)\,C_\chi(t - \tau) \tag{25}$$

where $C_\chi(t) = (\hat{\chi}(t),\hat{\chi})(\hat{\chi},\hat{\chi})^{-1}$, the Kubo canonical correlation.

The kernel $\tilde{k}(t)$ is itself a time correlation function,

$$\tilde{k}(\tau) = (e^{i\hat{Q}\hat{L}t} i\hat{L}\hat{\chi}, i\hat{L}\hat{\chi})(\hat{\chi},\hat{\chi})^{-1} \tag{22}$$

$\tilde{k}(t)$ is the time-dependent friction of the Generalized Langevin equation. It also is called the memory function.

Note that $\tilde{k}(t)$ evolves by unnatural dynamics, $i\hat{Q}\hat{L}$, denoted by the superscript ˜, as compared to ordinary dynamics, $i\hat{L}$. Thus $\tilde{k}(t)$, evolving in the subspace defined by Q, decays to zero on the time scale τ_{MIC}.

2.4 *Structure of the rate kernel.* Comparison of eq. 24 with the phenomenological rate law of eq. 7 identifies eq. 24 as a rate law derived from microscopic theory. Up to this point, no approximations have been made, and eq. 24 is exact. However, eq. 24 is unsatisfying, as the microscopic picture of the rate contant k of eq. 7 remains unclear: eq. 24 is an integro-differential equation (a convolution); and $\tilde{k}(t)$ obeys unnatural dynamics. Fortunately, these difficulties can be remedied by making several approximations that introduce negligible error.

Because $\tilde{k}(t)$ decays on the time scale τ_{MIC} and $\hat{\chi}$ evolves on the much longer time scale τ_{RXN}, for times t^*, $\tau_{MIC} << t^* << \tau_{RXN}$, $\bar{\chi}(t)$ is effectively constant, and we can write the rhs of eq. 24 as a product:

$$\frac{d\bar{\chi}(t)}{dt} \approx -\left[\int_0^{t^*} d\tau\ \tilde{k}(\tau)\right]\bar{\chi}(t) \tag{29}$$

Comparing eqs. 29 and 7 and noting that the upper limit t^* of the integral of eq. 29 can be extended to infinity, since by time t^* the integrand will have decayed to zero, we can identify the phenomenological rate constant of eq. 7 as

$$k \approx \int_0^{\infty} d\tau\ \tilde{k}(\tau) \tag{30}$$

It is convenient to define the function

$$\tilde{K}(t) = \int_0^t d\tau\ \tilde{k}(\tau) = (e^{i\hat{Q}\hat{L}t}\hat{\chi}, i\hat{L}\hat{\chi})(\hat{\chi},\hat{\chi})^{-1} \tag{27}$$

For times greater than τ_{MIC}, $\tilde{K}(t)$ is constant and the rate constant

$$k \approx \tilde{K}(\infty) \tag{27}$$

We now pass from projected dynamics to ordinary dynamics, $i\hat{Q}\hat{L} \rightarrow i\hat{L}$, by defining the ordinary-dynamics variables

$$K(t) = (\hat{\chi}(t), i\hat{L}\hat{\chi})(\hat{\chi},\hat{\chi})^{-1} \tag{33}$$

and

$$k(t) = (i\hat{L}\hat{\chi}(t), i\hat{L}\hat{\chi})(\hat{\chi},\hat{\chi})^{-1} \tag{34}$$

The tilde is dropped for ordinary dynamics.

Analysis of eqs 22, 27, 33 and 34 shows that for for times $t >> \tau_{MIC}$, and for ordinary dynamics,

$$K(t) \approx ke^{-kt} \tag{43}$$

For times t^*, $\tau_{MIC} << t^* << \tau_{RXN}$, $K(t^*)$ is approximately constant, and in this plateau region, extending from time τ_{MIC} to τ_{RXN}, we can identify the phenomenological rate constant as being

$$k \approx K(t^*) = (\hat{\chi}(t^*), i\hat{L}\hat{\chi})(\hat{\chi},\hat{\chi})^{-1} \tag{44}$$

The principal result of all the foregoing analysis is the expression of eq. 44 for the rate constant. We have now identified the phenomenological rate constant with a microscopic time correlation function, and the link between theory and experiment is complete. The picture is now clear: the macroscopic rate constant k is equal to the derivative of the time correlation function for fluctuations of the progress variable $\hat{\chi}$, evaluated for times t^* in the plateau region. Because eq. 44 is for ordinary dynamics, the time correlation function is accessible to analysis and to modeling by molecular dynamics.

The approximations made to this point, in passing from eq. 24 to 29, from eq. 33 to 43, and from eq. 43 to 44, all depend on the time-scale separation of τ_{RXN} from τ_{MIC}. For reactions with τ_{RXN} > ps, the error has been shown to be negligible. If there is no plateau region, then eq. 24 or eq 25 must be used.

We note that eq. 43 is an expression of the Onsager principle relating microscopic and macroscopic dynamics: for a system near equilibrium, on average the microscopic dynamics of the decay of large fluctuations in a variable (the dynamics of decay of its time correlation function), are the same as the dynamics of relaxation of the variable to its equilibrium value in a macroscopic system.

3. - **Classical systems.**

The above expressions hold when modified for classical dynamics and averaging. Specifically,

$$K(t) = <\dot{\chi}\chi(t)><\chi\chi>^{-1} \tag{49}$$

$$= -\frac{d}{dt}<\chi\chi(t)><\chi\chi>^{-1}$$

As an example, consider a system with a single reactive degree of freedom q and a double-well potential $W(q)$ (Fig. 2 of Kapral et al.). For this system, the progress variable is determined by whether the value of q corresponds to well A or well B, to the left or the right of the barrier top at $q^{\ddagger}$:

$$\chi(q) = -(\theta(q - q^{\ddagger}) - <\theta(q - q^{\ddagger}))> \tag{50}$$

From eqs. 49 and 50, with the operations given in *great* detail,

$$\begin{aligned}
K(t) &= -\frac{d}{dt} < \chi\chi(t) > < \chi\chi >^{-1} \\
&= -\frac{d}{dt}\left[< \theta(q-q^{\ddagger})\,\theta(q(t)-q^{\ddagger}) > - < \theta(q-q^{\ddagger}) >^{2} \right] < \chi\chi >^{-1} \\
&= - < \theta(q-q^{\ddagger})\,\dot{\theta}(q(t)-q^{\ddagger}) > < \chi\chi >^{-1} \\
&= < \dot{\theta}(q-q^{\ddagger})\,\theta(q(t)-q^{\ddagger}) > < \chi\chi >^{-1} \\
&= < \dot{q}\,\delta(q-q^{\ddagger})\,\theta(q(t) - q^{\ddagger}) > < \chi\chi >^{-1} && (51) \\
&= < \delta(q-q^{\ddagger}) > < \dot{q}\,\theta(q(t) - q^{\ddagger}) >_{q^{\ddagger}} < \chi\chi >^{-1} \\
&= \frac{1}{x_B\,(1 - x_B)}\, P(q^{\ddagger})\ < \dot{q}\,\theta(q(t) - q^{\ddagger}) >_{q^{\ddagger}} && (51a)
\end{aligned}$$

where

$$\begin{aligned}
< \chi\chi(t) > &= < (\theta(q-q^{\ddagger}) - < \theta(q-q^{\ddagger}) >)\cdot(\theta(q(t)-q^{\ddagger}) - < \theta(q-q^{\ddagger}) >) > \\
&= < \theta(q-q^{\ddagger})\,\theta(q(t)-q^{\ddagger}) > - < \theta(q-q^{\ddagger}) >^{2}
\end{aligned}$$

$$\begin{aligned}
\frac{d}{dt}\theta(q(t) - q^{\ddagger}) &= \frac{d}{dq}\theta(q(t) - q^{\ddagger})\ \frac{d}{dt}(q(t) - q^{\ddagger}) \\
&= \delta(q(t)-q^{\ddagger})\,\dot{q}(t)
\end{aligned}$$

$$\begin{aligned}
< \chi\chi > &= < (\theta(q-q^{\ddagger}) - < \theta(q-q^{\ddagger}) >)^{2} > \\
&= < \theta(q-q^{\ddagger})^{2} > - < \theta(q-q^{\ddagger}) >^{2} \\
&= < \theta(q-q^{\ddagger}) > - < \theta(q-q^{\ddagger}) >^{2} = x_B\,(1 - x_B)
\end{aligned}$$

$\theta(x)$ = *Heaviside function: 1 if x > 0, 0 otherwise*

$P(q^{\ddagger}) = < \delta(q-q^{\ddagger}) >$
= *normalized probability density for* $q = q^{\ddagger}$

$<\ldots>_{q^{\ddagger}}$ = *averaging of ... with q initially constrained at* $q^{\ddagger}$

Eq. 51a is eq. 17 of Chandler (1998).

Eq. 18 of Chandler (1998) for the TST theory rate constant is obtained for $t \rightarrow 0^+$:

$$
\begin{aligned}
k^{TST} &= \lim_{\varepsilon \rightarrow 0^+} K(\varepsilon) && (52)\\
&= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{x_B\ (1\ -\ x_B)}\ P(q^{\ddagger})\ <\dot{q}\theta(q(\varepsilon)\ -\ q^{\ddagger})>_{q^{\ddagger}}\\
&= \frac{1}{x_B\ (1\ -\ x_B)}\ P(q^{\ddagger})\ <\dot{q}\theta(\dot{q})>_{q^{\ddagger}}\\
&= \frac{1}{x_B\ (1\ -\ x_B)}\ P(q^{\ddagger})\ \frac{<|\dot{q}|>}{2} && (54)
\end{aligned}
$$

Eq. 54 for the TST rate constant can be expressed in a form more familiar from our previous treatment of TST, by evaluating $P(q^{\ddagger})$ and $<|\dot{q}|>$. For convenience, we assume that the work function (free energy) $W(q)$, with minima at q_A and q_B, has the same shape (same frequency, or force constant) for both wells and is harmonic, i.e., near q_A, $W(q) = W''(q - q_A)$ with $W'' = m\omega_A^2$, and similarly near q_B. $W(q_A)$ need not equal $W(q_B)$.

$$
\begin{aligned}
P(q^{\ddagger}) &= \frac{e^{-W(q^{\ddagger})/kT}}{\int_{A+B} dq\ e^{-W(q)/kT}}\\
&= \frac{e^{-(W(q^{\ddagger}) - W(q_A))/kT}}{Q_A\ +\ Q_B \cdot e^{-(W(q_{B)} - W(q_{A))/kT}}}\\
&= (1\ -\ x_B)\ \frac{e^{-\Delta W(q^{\ddagger})/kT}}{(1\ -\ x_B)Q_A\ +\ x_B Q_B}\\
&= (1\ -\ x_B)\ \frac{e^{-\Delta W^{\ddagger}/kT}}{Q_A}
\end{aligned}
$$

giving

$$
P(q^{\ddagger})\ =\ (1\ -\ x_B)\ \frac{\omega_A}{\sqrt{2\pi}} \left[\frac{m}{kT} \right]^{1/2} e^{-\Delta W^{\ddagger}/kT}
$$

for

$$Q_A = Q_B$$

$$= \int_A dq \; e^{-(W(q) - W(q_A))/kT}$$

$$= \int_A dq \; e^{-m\omega_A^2 (q - q_A^2)/2kT} = \left[\frac{2\pi kT}{m} \right]^{1/2} \frac{1}{\omega_A}$$

Also,

$$\frac{<|\dot{q}|>}{2} = \frac{\int_{-\infty}^{+\infty} dp \; \frac{|p|}{m} \; e^{\frac{-p^2}{2mkT}}}{\int_{-\infty}^{+\infty} dp \; e^{\frac{-p^2}{2mkT}}} = \left[\frac{kT}{2\pi m} \right]^{1/2}$$

Evaluating eq. 54,

$$k^{TST} = \frac{1}{x_B} \frac{\omega_A}{2\pi} e^{-\Delta W^{\ddagger}/kT}$$

Noting that for a double well potential the relaxation rate constant $k = k_f + k_r = k_f / x_B$, we obtain Hynes (1988) eq. 4:

$$k_f^{TST} = \frac{\omega_A}{2\pi} e^{-\Delta W^{\ddagger}/kT} \qquad \text{(Hynes-4)}$$

COMMENT: Chandler's theory, the reactive flux method, is important:

(1) It is firmly grounded in physical theory, with precisely-stated approximations, the effect of which can be evaluated.

(2) The expression for the rate constant (eq. 44 or 49) can be evaluated by computer simulation.

(3) Transition State theory is a limiting case of reactive flux theory (see eq. Hynes-4). TST is placed on a firm and clear theoretical footing, without the need for tricks and special assumptions to solve the mathematical model. Kramers theory also does this, but perhaps with less elegance and generality. Note that TST gives always an upper bound on the true rate.

(4) Reactive flux theory makes contact with Kramers theory and Grote-Hynes theory through the Generalized Langevin equation, i.e., through the memory function $\tilde{k}(t)$ and the corresponding ordinary-dynamics function $k(t)$ of eqs. 22 and 34. However, I do not know of a derivation of an explicit statement of this relationship.

The last point above points to the principal drawback of reactive flux theory: the correlation function expression for the dynamics of a progress variable is easy to work with computationally but difficult to work with analytically, as in reduction to the expressions of Kramers theory or to those of the multi-dimensional extensions of TST. Kramers theory and most other theories work directly with the dynamics of phase-space variables and lead to expressions for a rate constant that can be evaluated without the need for numerical methods. Reactive flux theory depends upon evaluation at a plateau time, t^*, which is difficult to explore other than by numerical methods. This difficulty is inherent in the nature of a chemical reaction: the system changes in a finite time, τ_{RXN}, which prevents the extrapolation to infinite time/zero frequency that is so effective in analysis of other transport properties by use of the Kubo and Mori-Zwanzig methods.