

# Foundations of Chemical Kinetics Lecture 14: The master equation, IVR and rate equations

Marc R. Roussel

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# Transition rates

- Suppose that  $P_s(t)$  is the probability that a system is in a state  $s$  at time  $t$ .
- The states are members of a set  $\mathcal{S}$  of allowed states.
- Transitions occur randomly between the different states.
- For each pair of states  $r$  and  $s$ , there is a **transition rate**  $w_{rs}$  such that, if the system is in state  $r$  at time  $t$ , the probability that the system jumps to state  $s$  during the subsequent time interval  $dt$  is  $w_{rs} dt$ .

# Transition probabilities

## Markov property

- In general,  $w_{rS}$  can depend on the history of the system, i.e.  $w_{rS}$  can depend on how long the system has been in state  $r$ , which state it came from before that, etc.
- In a **Markov process**,  $w_{rS}$  does not depend on the history.
- We additionally limit ourselves to homogeneous Markov processes in which  $w_{rS}$  does not depend on  $t$ .

## Derivation of the master equation

- The master equation gives us the time evolution of the probabilities  $P_s(t)$ .
- The probability of being in state  $s$  at time  $t + dt$  can be written as follows:

$$P_s(t + dt) = P_s(t) + \sum_{r \neq s} w_{rs} P_r(t) dt - \sum_{r \neq s} w_{sr} P_s(t) dt$$

- The first term is the probability that the system was already in state  $s$  at time  $t$ .
- The terms in the first sum represent the probability that the system *was* in state  $r$  at time  $t$  ( $P_r(t)$ ) *and* jumped into state  $s$  during the interval  $dt$  ( $w_{rs} dt$ ).  
The sum includes all states from which the system could have come.
- The final sum does the same thing as above but for jumps *out* of state  $s$ .

## Derivation of the master equation

(continued)

$$P_s(t + dt) = P_s(t) + \sum_{r \neq s} w_{rs} P_r(t) dt - \sum_{r \neq s} w_{sr} P_s(t) dt$$

- Rearrange:

$$\frac{P_s(t + dt) - P_s(t)}{dt} = \sum_{r \neq s} w_{rs} P_r(t) - \sum_{r \neq s} w_{sr} P_s(t)$$

- In the limit as  $dt \rightarrow 0$ , the left-hand side becomes a derivative:

$$\frac{dP_s}{dt} = \sum_{r \neq s} w_{rs} P_r - \sum_{r \neq s} w_{sr} P_s$$

This is the **master equation**.

(The argument  $(t)$  was dropped because all terms are now evaluated at time  $t$ .)

## Alternative interpretation

- If we have a gas containing a large number of molecules,  $P_s$  might represent the probability that a randomly selected molecule is in quantum state  $s$ .
- For a large number of molecules, we should have  $N_s = N_{\text{total}} P_s$ .
- Thus, the master equation could also be written

$$\frac{dN_s}{dt} = \sum_{r \neq s} w_{rs} N_r - \sum_{r \neq s} w_{sr} N_s$$

# The master equation and the equilibrium distribution

- We rewrite the master equation slightly:

$$\frac{dP_s}{dt} = \sum_{r \neq s} (w_{rs}P_r - w_{sr}P_s)$$

- At equilibrium,  $dP_s/dt = 0$ . Thus

$$\sum_{r \neq s} \left( w_{rs}P_r^{(\text{eq})} - w_{sr}P_s^{(\text{eq})} \right) = 0 \quad \forall s$$

- One solution of this system of equations satisfies **detailed balance**, i.e. each pair of terms appearing therein individually equals zero:

$$w_{rs}P_r^{(\text{eq})} - w_{sr}P_s^{(\text{eq})} = 0$$

# The master equation and the equilibrium distribution

(continued)

- The detailed balance condition can be rewritten

$$\frac{P_r^{(\text{eq})}}{P_s^{(\text{eq})}} = \frac{w_{sr}}{w_{rs}}$$

- At equilibrium, the probabilities should obey a Boltzmann distribution, so

$$\frac{w_{sr}}{w_{rs}} = \exp\left(-\frac{\epsilon_r - \epsilon_s}{k_B T}\right)$$

where  $r$  and  $s$  label **individual quantum states** of the system.

- Alternatively, if we want  $r$  and  $s$  to label energy levels, we would have

$$\frac{w_{sr}}{w_{rs}} = \frac{g_r}{g_s} \exp\left(-\frac{\epsilon_r - \epsilon_s}{k_B T}\right)$$



# The master equation and the equilibrium distribution

## Comments

$$\frac{w_{sr}}{w_{rs}} = \frac{g_r}{g_s} \exp\left(-\frac{\epsilon_r - \epsilon_s}{k_B T}\right)$$

- This equation only fixes the ratio of the transition rates.
  - The actual values of the transition rates will depend on a number of factors, including the concentrations of collision partners.
  - Many different functional forms for the transition rates are compatible with this ratio.
- Because the transition rates decrease exponentially with increasing energy difference, it is often a good approximation to only consider transitions between adjacent energy levels (Landau-Teller approximation).

# The master equation and the equilibrium distribution

## Comments

$$\frac{w_{SR}}{w_{RS}} = \frac{g_r}{g_s} \exp\left(-\frac{\epsilon_r - \epsilon_s}{k_B T}\right)$$

- If  $\epsilon_r > \epsilon_s$ , the Boltzmann factor is smaller than 1.  
If additionally  $g_r = g_s$ , then  $w_{SR} < w_{RS}$ , i.e. 'downward' transitions will be more frequent than upward transitions.
- This rate difference shrinks as the gap between energy levels decreases.  
High vibrational states usually have small energy level differences, so once a molecule has gained sufficient vibrational energy, there is less of a bias towards returning to lower energies.

## Example: A two-level system

- For a two-level system, the master equation is

$$\begin{aligned}\frac{dP_1}{dt} &= w_{21}P_2 - w_{12}P_1 \\ \frac{dP_2}{dt} &= w_{12}P_1 - w_{21}P_2\end{aligned}$$

- Note that

$$\frac{dP_1}{dt} + \frac{dP_2}{dt} = \frac{d}{dt}(P_1 + P_2) = 0$$

so that  $P_1 + P_2$  is a constant, which must be  $P_1 + P_2 = 1$ .

Thus

$$\frac{dP_1}{dt} = w_{21}(1 - P_1) - w_{12}P_1$$

## Example: A two-level system

(continued)

$$\frac{dP_1}{dt} = w_{21}(1 - P_1) - w_{12}P_1$$

$$\frac{dP_1}{w_{21} - P_1(w_{21} + w_{12})} = dt$$

$$\therefore \int_{P_1(0)}^{P_1(t)} \frac{dP_1}{w_{21} - P_1(w_{21} + w_{12})} = \int_0^t dt' = t$$

$$\therefore t = -\frac{1}{w_{21} + w_{12}} \ln [w_{21} - P_1(w_{21} + w_{12})]_{P_1(0)}^{P_1(t)}$$

$$\therefore -t(w_{21} + w_{12}) = \ln \left( \frac{w_{21} - P_1(t)(w_{21} + w_{12})}{w_{21} - P_1(0)(w_{21} + w_{12})} \right)$$

$$\therefore P_1(t) = \frac{w_{21}}{w_{21} + w_{12}} \left( 1 - e^{-t(w_{21} + w_{12})} \right) + P_1(0) e^{-t(w_{21} + w_{12})}$$

## Example: A two-level system

(continued)

- A slight rewrite of the solution gives

$$P_1(t) = \frac{1 - e^{-t(w_{21}+w_{12})}}{1 + w_{12}/w_{21}} + P_1(0) e^{-t(w_{21}+w_{12})}$$

- Now using the Boltzmann detailed balance condition and setting the ground-state energy to zero, we get

$$\begin{aligned} P_1(t) &= \frac{1 - e^{-t(w_{21}+w_{12})}}{1 + \frac{g_2}{g_1} \exp\left(-\frac{E_2}{k_B T}\right)} + P_1(0) e^{-t(w_{21}+w_{12})} \\ &= \frac{g_1 (1 - e^{-t(w_{21}+w_{12})})}{g_1 + g_2 \exp\left(-\frac{E_2}{k_B T}\right)} + P_1(0) e^{-t(w_{21}+w_{12})} \\ &= \frac{g_1}{Q} \left(1 - e^{-t(w_{21}+w_{12})}\right) + P_1(0) e^{-t(w_{21}+w_{12})} \end{aligned}$$

## Example: A two-level system

(continued)

$$P_1(t) = \frac{g_1}{Q} \left( 1 - e^{-t(w_{21}+w_{12})} \right) + P_1(0) e^{-t(w_{21}+w_{12})}$$

Limits:

- As  $t \rightarrow 0$
- As  $t \rightarrow \infty$

Relaxation time:

(Time required for distance to equilibrium to decrease by a factor of  $1/e$ )

## Solving the master equation in general

$$\frac{dP_s}{dt} = \sum_{r \neq s} w_{rs} P_r - \sum_{r \neq s} w_{sr} P_s$$

- The master equation is a set of **linear** differential equation in the  $P_i$ 's, so for systems with a finite number of states, it is in principle always solvable.
- In practice, it's not so simple because of the large number of variables.

## Solving the master equation in general

(continued)

$$\frac{dP_s}{dt} = \sum_{r \neq s} w_{rs} P_r - \sum_{r \neq s} w_{sr} P_s$$

- The solution requires the calculation of the eigenvalues and eigenvectors of the matrix of coefficients

$$W = \begin{bmatrix} -w_{11} & w_{21} & \dots & w_{n1} \\ w_{12} & -w_{22} & \dots & w_{n2} \\ \vdots & \vdots & \ddots & \vdots \\ w_{1n} & w_{2n} & \dots & -w_{nn} \end{bmatrix}$$

where  $w_{ii} = \sum_{j \neq i} w_{ij}$ .



## Solving the master equation in general

(continued)

- Solution expressible as a sum of terms involving  $e^{\lambda_i t}$ , where the  $\lambda_i$ 's are the eigenvalues
- For the master equation,  $\lambda_i < 0 \forall i$ .
- Solving large eigenvalue problems can be difficult.
  - There are usually large gaps in the eigenvalue spectrum such that we get a good approximation to the long-term behavior by keeping only a few of the terms (those with the smallest  $\lambda_i$  values).

## Solving the master equation in general

(continued)

Alternatives:

- Direct numerical solution of master equation
  - Because of the wide range of eigenvalues and potentially large number of variables, these problems can be hard to solve numerically.
- Simulation of the underlying random process
  - Easier to implement, but because we need to run lots of **realizations** (independent simulations) to get statistics, this can still take a long time.

## Cumulative probability distributions

- Suppose that we have a probability distribution, say  $P_s$ , which gives the probability that a particular variable has the value  $s$ .
- The **cumulative probability distribution** is the probability that  $s$  is less than or equal to some particular value. In other words, the cumulative distribution is defined by

$$F(S) = P(s \leq S) = \sum_{s \leq S} P_s$$

- The complementary cumulative distribution is the probability that  $s$  is greater than some value. Thus, it is defined by

$$\bar{F}(S) = P(s > S) = 1 - F(S)$$

## Cumulative distribution of a continuous variable

- If  $t$  is a continuous variable, instead of probabilities, we have a probability density  $p(t)$  such that

$$P(a \leq t \leq b) = \int_a^b p(t) dt$$

- The **cumulative distribution function** (cdf) is obtained by integration:

$$F(T) = P(t \leq T) = \int_{\mathcal{L}}^T p(t) dt$$

where  $\mathcal{L}$  is the lower limit of  $t$  (often either 0 or  $-\infty$ ).

- By the fundamental theorem of calculus, the probability density can be recovered from the cdf by differentiation:

$$p(t) = \left. \frac{dF}{dT} \right|_{T=t}$$

## A microcanonical master equation treatment of reaction from a set of privileged (transition) states

- We're going to calculate the RRK rate constant  $k_{2K}$ , which involves intramolecular vibrational relaxation leading to reaction once a molecule accumulates sufficient energy in the reactive mode.
- During IVR, a molecule wanders among a set of equal-energy states.
- Given that the states are of equal energy, we have

$$\frac{w_{sr}}{w_{rs}} = \exp\left(-\frac{E_r - E_s}{k_B T}\right) = 1$$

We can therefore set  $w_{sr} = w_{rs} = w$  for all  $(r, s)$ .

## A microcanonical master equation treatment. . .

(continued)

- A molecule reacts (dissociates or isomerizes) as soon as it hits a state in which the reactive mode has enough energy. These **reactive states** correspond to  $A^\ddagger$  in RRK theory.
- Accordingly, the system cannot return from one of the reactive states.  
(Certainly true for dissociations, less clear for isomerizations)
- Mathematically, the reactive states are **absorbing states**.
- The average time required to reach a reactive state is the inverse of the rate constant.

## A microcanonical master equation treatment. . .

(continued)

- Let  $\mathcal{N}$  be the set of non-reactive states, and  $\mathcal{R}$  be the set of reactive states.
- If, as in RRK theory, the energy  $E$  consists of  $j$  quanta shared over  $s$  oscillators, the degeneracy of this energy level is

$$G^* = \frac{(j + s - 1)!}{j!(s - 1)!}$$

- Again as in RRK theory, if we need at least  $m$  quanta in the reactive mode in order to react, the degeneracy of the set of reactive states is

$$G^\ddagger = \frac{(j - m + s - 1)!}{(j - m)!(s - 1)!}$$

- The non-reactive set has size  $G_{\mathcal{N}} = G^* - G^\ddagger$ .

# A microcanonical master equation treatment...

(continued)

- The master equation is

$$\frac{dP_n}{dt} = w \sum_{n' \in \mathcal{N}} (P_{n'} - P_n) - G^\ddagger w P_n \quad \forall n \in \mathcal{N}$$

$$\frac{dP_r}{dt} = w \sum_{n' \in \mathcal{N}} P_{n'} \quad \forall r \in \mathcal{R}$$

- The last term in  $dP_n/dt$  is  $-\sum_{n' \in \mathcal{R}} w P_{n'}$  ( $G^\ddagger$  terms for transfer from state  $n$  to the reactive set).



# A microcanonical master equation treatment...

(continued)

$$\frac{dP_n}{dt} = w \sum_{n' \in \mathcal{N}} (P_{n'} - P_n) - G^\ddagger w P_n \quad \frac{dP_r}{dt} = w \sum_{n' \in \mathcal{N}} P_{n'}$$

- Define  $P_{\mathcal{N}}$  and  $P_{\mathcal{R}}$ , the probability that the system is, respectively, in the non-reactive or reactive set:

$$P_{\mathcal{N}} = \sum_{n \in \mathcal{N}} P_n \quad P_{\mathcal{R}} = \sum_{r \in \mathcal{R}} P_r$$

- These equations can be rewritten

$$\begin{aligned} \frac{dP_n}{dt} &= wP_{\mathcal{N}} - wG_{\mathcal{N}}P_n - wG^\ddagger P_n & \forall n \in \mathcal{N} \\ \frac{dP_r}{dt} &= wP_{\mathcal{N}} & \forall r \in \mathcal{R} \end{aligned}$$

# A microcanonical master equation treatment...

(continued)

- Differentiating the definitions of  $P_{\mathcal{N}}$  and  $P_{\mathcal{R}}$  with respect to time, we get

$$\frac{dP_{\mathcal{N}}}{dt} = \sum_{n \in \mathcal{N}} \frac{dP_n}{dt}$$

$$\frac{dP_{\mathcal{R}}}{dt} = \sum_{r \in \mathcal{R}} \frac{dP_r}{dt}$$

- Therefore

$$\begin{aligned} \frac{dP_{\mathcal{N}}}{dt} &= \sum_{n \in \mathcal{N}} wP_{\mathcal{N}} - \sum_{n \in \mathcal{N}} wG_{\mathcal{N}}P_n - \sum_{n \in \mathcal{N}} wG^{\ddagger}P_n \\ &= wG_{\mathcal{N}}P_{\mathcal{N}} - wG_{\mathcal{N}}P_{\mathcal{N}} - wG^{\ddagger}P_{\mathcal{N}} = -wG^{\ddagger}P_{\mathcal{N}} \end{aligned}$$

$$\frac{dP_{\mathcal{R}}}{dt} = \sum_{r \in \mathcal{R}} wP_{\mathcal{N}} = wG^{\ddagger}P_{\mathcal{N}}$$

## A microcanonical master equation treatment. . .

(continued)

- Assuming that all states of energy  $E$  are equally likely, the probability of obtaining a state in  $\mathcal{N}$  when the molecule is first energized is  $P_{\mathcal{N}}(0) = G_{\mathcal{N}}/G^*$ .  
A fraction  $G^{\ddagger}/G^*$  of the molecules reacts immediately on energization.
- Taking this into account raises some technical difficulties because the cumulative distribution of reaction times is then discontinuous across  $t = 0$ .  
(It jumps from 0 for  $t < 0$  to  $G^{\ddagger}/G^*$  at  $t = 0$ .)
- It is possible to treat this case properly using the Heaviside function and its derivative, the Dirac delta function.
- To avoid these complications, note that  $G^{\ddagger}/G^*$  will normally be small. Thus, assume that  $P_{\mathcal{N}}(0) = 1$ .

# A microcanonical master equation treatment...

(continued)

- The rate equation for  $P_{\mathcal{N}}$  subject to this initial condition is easy to solve:

$$P_{\mathcal{N}} = e^{-wG^\ddagger t}$$

- Since  $P_{\mathcal{N}} + P_{\mathcal{R}} = 1$ , we have

$$P_{\mathcal{R}} = 1 - P_{\mathcal{N}} = 1 - e^{-wG^\ddagger t}$$

# A microcanonical master equation treatment. . .

(continued)

- What is  $P_{\mathcal{R}}$ ?
  - It is the probability that, by time  $t$ , an energized molecule has reacted.
  - In other words,  $P_{\mathcal{R}}$  is the cumulative probability distribution of the reaction time.
- To get the probability density of the reaction time, we differentiate  $P_{\mathcal{R}}$ :

$$p_{\mathcal{R}}(t) = wG^{\ddagger} e^{-wG^{\ddagger}t}$$

- This can also be thought of as the distribution of lifetimes of the energized molecules.

# A microcanonical master equation treatment...

(continued)

- Recall (from lecture 3): The average of  $f(t)$ , denoted  $\langle f \rangle$ , is calculated by

$$\langle f \rangle = \int_0^{\infty} f(t)p(t) dt$$

- In this case, the average reaction time,  $\langle t \rangle$ , is

$$\begin{aligned} \langle t \rangle &= \int_0^{\infty} tp_{\mathcal{R}}(t) dt \\ &= wG^{\ddagger} \int_0^{\infty} te^{-wG^{\ddagger}t} dt \\ &= (wG^{\ddagger})^{-1} \end{aligned}$$

- The rate constant is therefore

$$k_{2K} = \langle t \rangle^{-1} = wG^{\ddagger}$$

# A microcanonical master equation treatment. . .

(continued)

$$k_{2K} = wG^\ddagger$$

- This treatment predicts a rate constant proportional to  $G^\ddagger$ , just like the RRK treatment.
- No dependence on  $G^*$
- Our new expression predicts something very different from RRK: It says that the rate constant depends on how fast IVR takes place, but not on how fast the molecule moves through the transition state.
- This is one way to rationalize extremely large rate constants for gas-phase unimolecular reactions.